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Nanocrystalline Titania: Controlling Physical Properties
and Photocatalytic Behavior

by

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Abstract

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This dissertation describes a hydrothermal method for synthesizing titanium dioxide nanocrystals with controllable physical properties and explores the influence of such properties on the material’s photocatalytic efficiency. The preparation of nanoscale titania from an alkoxide precursor in ethanol under mild hydrothermal conditions yields highly crystalline, thermally stable, phase-pure anatase dots whose sizes can be fine-tuned through adjustment of reaction temperature, precursor concentration, and water-to-alkoxide ratio. By optimizing the synthetic conditions, one may obtain grain sizes as small as 5.5 nm and surface areas up to 250 m² g⁻¹. The importance of various physical properties in determining the photocatalytic performance of nanocrystalline titania is investigated and clarified using photodegradation of an azo dye as a model reaction. Experimental photocatalytic activities, as quantified by dye half-life and Langmuir-Hinshelwood rate constants, confirm that anatase is an inherently superior photocatalyst to rutile and that activity enhancement due to anatase-rutile synergy in mixed-phase catalysts is contingent upon other factors such as the nature of the anatase-rutile interface. Also, it is shown for the first time that the shape of a titania nanocrystal significantly affects its photocatalytic efficiency. Specifically, rodlike anatase nanocrystals with predominantly (1 0 1) surfaces perform poorly as photocatalysts because the non-dissociative adsorption of water to these surfaces prevents efficient generation of the OH• radicals thought to be essential for photocatalytic oxidation.
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Upon completing my dissertation, it occurred to me that on balance, despite my occasional indulgences in some good old-fashioned cathartic complaining, I had actually enjoyed writing it. I have long viewed writing as more exciting and rewarding than grueling and punishing, and for this I must credit the uniformly excellent English teachers I have had over the years; apart from their scrupulous attention to teaching correct grammar and writing skills in general (instruction for which I have been mentally thanking them almost daily during the last several months), they possessed such a powerful and unabashed love for the English language and for the communication of ideas that I couldn’t help but be excited about writing when I was in their classes. If it hadn’t been for these teachers’ influence and instruction, I would probably have felt burned out instead of exhilarated by the time I finished writing this thesis. I cannot thank them enough, though I will certainly try.

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Table of Contents

Introductory remarks ................................................. 1

Chapter 1. Structures, basic properties, and applications of crystalline titanium dioxide at the bulk and nanometer scales

1.1. Major polymorphs of TiO$_2$: structure and stability .... 4
1.2. Important properties of TiO$_2$ .................................. 7
1.3. Applications of TiO$_2$ .............................................. 9
1.4. Summary ............................................................ 10
References ............................................................... 10

Chapter 2. Literature review I: Synthesis of titanium dioxide nanocrystals ....................................................... 12

2.1. Introduction ......................................................... 12
2.2. Aerosol pyrolysis .................................................. 13
2.3. Non-hydrolytic solution-phase reactions ...................... 16
2.4. Hydrolytic solution-phase reactions ........................... 19
2.5. Summary and relevance to present work ...................... 36
References ............................................................... 37

Chapter 3. Hydrothermal synthesis and characterization of anatase TiO$_2$ nanocrystals with ultra-high surface area

3.1. Introduction ......................................................... 45
3.2. Experimental ...................................................... 46
3.3. Results and discussion .......................................... 49
3.4. Summary and future work 63
3.5. References 64

Chapter 4. Growth modeling of monodisperse TiO$_2$ nanoparticles in solution 66

4.1. Introduction 66
4.2. The single-particle growth model 67
4.3. Application of the single-particle growth model to hydrothermally derived anatase nanocrystals 76
4.4. Proposed method for estimating thermodynamic and kinetic parameters from initial growth rates 82
4.5. Summary and future work 86

References 87

Chapter 5. Literature review II: Heterogeneous photocatalysis with titanium dioxide 89

5.1. Introduction 89
5.2. Basic principles of TiO$_2$-mediated photooxidation in aqueous solutions 92
5.3. Factors affecting the photocatalytic activity of TiO$_2$ 99
5.4. Summary and relevance to present work 112

References 114

Chapter 6. Photodegradation of Congo Red with nanoscale TiO$_2$: Influence of grain size, surface area, phase composition, and particle morphology on photocatalytic activity 122

6.1. Introduction 122
6.2. Experimental 126
6.3. Data analysis 138
6.4. Results and discussion

6.5. Summary and future work

References

Appendix. MATLAB code for modeling the growth of monodisperse anatase nanocrystals under hydrothermal conditions
Figures and Tables

Figure 1.1. The crystal structures of anatase, rutile, and brookite 5

Figure 2.1. Schematic diagram of an apparatus for aerosol pyrolysis 14

Figure 2.2. Influence of OH⁻ ligands on the crystallization of TiO₂ from hydrolytic reactions 23

Figure 2.3. Effect of tetramethylammonium cations (N(CH₃)₄⁺) on anatase nanocrystal growth 27

Figure 2.4. A bomb reactor used for hydrothermal crystallization in the Colvin research group 30

Figure 3.1. X-ray diffraction (XRD) spectra of hydrothermal anatase prepared at different temperatures 50

Figure 3.2. Effect of reaction temperature on grain size of hydrothermal anatase 52

Figure 3.3. Transmission electron micrographs (TEMs) of hydrothermal anatase 55

Figure 3.4. Effect of precursor concentration on grain size of hydrothermal anatase 56

Figure 3.5. Effect of hydrolysis ratio on grain size of hydrothermal anatase 57

Figure 3.6. Evolution of TiO₂ Raman spectra with hydrothermal reaction temperature 59

Figure 3.7. Evolution of TiO₂ differential thermal analysis (DTA) profiles with hydrothermal reaction temperature 61

Figure 3.8. XRD spectra for hydrothermal TiO₂ samples after heating to 600 °C 63

Figure 4.1. Schematic illustration of a spherical nanoparticle growing in solution 69

Figure 4.2. Experimental nano-anatase growth data fitted with the single-particle growth model 80

Figure 5.1. Elementary steps in TiO₂-mediated photooxidation 93

Figure 5.2. Proposed mechanisms for charge separation in anatase-rutile mixtures 109

Figure 6.1. The structure of Congo Red 126
Figure 6.2. Adsorption isotherms for Congo Red in the presence of different nano-
TiO$_2$ photocatalysts

Figure 6.3. The Luzchem Model 4-V photoreactor

Figure 6.4. UV-visible spectra of aqueous Congo Red in the presence of TiO$_2$ before
and after baselining

Figure 6.5. Procedure for estimating the initial rate of Congo Red degradation

Figure 6.6. Schematic illustration of Langmuir-Hinshelwood analysis

Figure 6.7. XRD spectra for nanocrystalline TiO$_2$ photocatalyst powders

Figure 6.8. TEM images of laboratory made nano-TiO$_2$ photocatalysts

Figure 6.9. Sample DTA profile of a nano-TiO$_2$ photocatalyst

Figure 6.10. Fourier transform infrared (FTIR) spectra for tetramethylammonium
hydroxide (TMAH) and a TiO$_2$ sample from which TMAH was removed by dialysis

Figure 6.11. Degradation profiles for aqueous Congo Red in the presence of various
nano-TiO$_2$ photocatalysts

Figure 6.12. Examples of Langmuir-Hinshelwood analysis of Congo Red
photodegradation data

Table 1.1. Structural parameters of anatase, rutile, and brookite

Table 2.1. Summary of synthetic routes to nanocrystalline TiO$_2$

Table 3.1. Grain sizes and specific surface areas for hydrothermal anatase

Table 4.1. Single particle growth model parameters calculated from experimental
growth data for anatase nanoparticles

Table 5.1. Physical properties affecting the photocatalytic activities of anatase and
rutile

Table 6.1. Synthetic conditions of nanosized TiO$_2$ photocatalysts

Table 6.2. Physical characteristics of nanosized TiO$_2$ photocatalysts

Table 6.3. Kinetic parameters for Congo Red photodegradation by various TiO$_2$
powders
Introductory remarks

During the last half century, an increasing amount of scientific research has been devoted to exploring and understanding the properties of titanium dioxide, both on a fundamental level and in the context of practical applications. Particularly exciting has been the discovery that TiO$_2$ is ideally suited for photocatalysis, a chemical process whose potential uses range from energy production to destruction of environmental contaminants such as organics and heavy metals. Interest in TiO$_2$ as a material for photocatalysis and similar applications has exploded with the recent advent of nanotechnology, which exploits the often dramatic differences between nanoscale materials and their bulk counterparts – differences that arise primarily because a large percentage of the atoms in a nanomaterial occupy surface sites, so that the surface properties of such materials play a much more important role in determining their physical and chemical properties than in bulk materials. Because photocatalysis with TiO$_2$ takes place on the surface of the material, it tends to proceed more efficiently when more surface sites are available. Thus it is not surprising that nanoscale TiO$_2$, with a high number of surface sites per gram, has been found to perform far better as a photocatalyst than bulk TiO$_2$.

Thanks to vigorous and extensive research on TiO$_2$ at the nanometer scale, it is now quite well characterized and represents a promising model system for studying the properties of engineered nanomaterials. Yet as is usually the case with scientific research, for every question that has been answered about nano-TiO$_2$ at least one new question has arisen. For the purposes of photocatalysis, the questions to be answered are all naturally related to a single overarching question: What are the physical characteristics that
maximize the material's photocatalytic efficiency? Which inevitably leads back to another overarching question: Once the desired physical properties are known, how does one prepare nano-TiO$_2$ samples that possess these properties?

In short, the object of any continued investigation into TiO$_2$ photocatalysts essentially comes down to the question of optimization through the tuning of material properties. This is currently a common theme among other studies on nanomaterials: scientists have the ability to make such materials and know what the materials can do; now the task is to make those materials with greater control over their properties so as to improve their performance.

Hence the motivation for the work described in this dissertation came from two different directions, as it were: the interest in TiO$_2$ as a case study for controlling the properties of nanomaterials through various synthetic conditions, and the interest in TiO$_2$ as an ideal photocatalyst. The former issue was addressed in a series of experiments in which nanocrystalline anatase-phase TiO$_2$ with tunable physical characteristics was prepared using a hydrothermal technique. The latter issue was then explored, using the photocatalytic degradation of an azo dye to probe the dependence of nano-TiO$_2$'s photocatalytic activity on various physical properties.

The organization of the thesis is as follows: first, the basic properties of TiO$_2$ and the existing methods for its preparation at the nanometer scale are reviewed in Chapters 1 and 2 respectively. Chapter 3 then describes the experiments in which hydrothermal anatase nanocrystals with controllable properties were prepared. Chapter 4 describes a simple theoretical model for predicting the average particle size in monodisperse systems of hydrothermally derived anatase dots, as well as a proposed method for estimating
kinetic and thermodynamic parameters governing nanocrystal formation in liquid phase processes. Chapter 5 provides a review of the basic principles of photocatalysis, along with what is currently known about the factors determining the photocatalytic activity of TiO$_2$. Finally, Chapter 6 presents the dye degradation experiments, which clarify some ambiguities regarding the influence of crystalline phase on photocatalytic activity and contribute new information regarding the importance of TiO$_2$ nanocrystal morphology in photocatalytic reactions.
Chapter 1

Structures, basic properties, and applications of crystalline titanium dioxide at the bulk and nanometer scales

1.1. Major polymorphs of TiO$_2$: structure and stability

Titanium dioxide, or titania as it is sometimes called, occurs naturally in three major crystal structures: rutile, anatase, and brookite. Rutile is the most common crystalline form of TiO$_2$ found in nature and has therefore been the most frequently studied and most thoroughly characterized polymorph at the bulk scale; in fact, the rutile (1 1 0) surface is regarded as a model system for studying the behavior of metal oxide surfaces.$^{1,2}$ However, anatase has recently received considerable attention because of its excellent performance in several catalytic and photovoltaic applications, particularly at the nanometer scale. Brookite, on the other hand, is rare in nature and has been the subject of comparatively few studies.$^3$

Both rutile and anatase have tetragonal unit cells, while brookite’s unit cell is orthorhombic. The three major polymorphs are illustrated in Figure 1.1 and their structural parameters are listed in Table 1.1. From Figure 1.1 it is apparent that anatase has a more open structure than rutile or brookite, so that the density of anatase (3.84 g cm$^{-3}$) is considerably lower than that of either of the other two phases (4.27 and 4.12 g cm$^{-3}$ for rutile and brookite respectively).$^4$

Generally in TiO$_2$ the titanium atoms exist in the 4+ oxidation state and assume sixfold (octahedral) coordination to neighboring oxygen atoms. Each oxygen in turn serves as a bridge between two titanium atoms. Each TiO$_2$ polymorph is based on a
Figure 1.1. The crystal structures of anatase, rutile, and brookite
Table 1.1. Structural parameters of anatase, rutile, and brookite

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal system</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>anatase</td>
<td>tetragonal</td>
<td>3.7845</td>
<td>3.7845</td>
<td>9.5143</td>
<td>Ti (0, 0, 0); O (0, 0, 0.208)</td>
</tr>
<tr>
<td>rutile</td>
<td>tetragonal</td>
<td>4.5937</td>
<td>4.5937</td>
<td>2.9587</td>
<td>Ti (0, 0, 0); O (0.305, 0.305, 0)</td>
</tr>
<tr>
<td>brookite</td>
<td>orthorhombic</td>
<td>9.1840</td>
<td>5.4470</td>
<td>5.1450</td>
<td>Ti (0.128, 0.098, 0.863); O1 (0.008, 0.147, 0.182); O2 (0.229, 0.110, 0.530)</td>
</tr>
</tbody>
</table>

different spatial arrangement of distorted [TiO_6] octahedra. The octahedra are linked entirely by edge sharing in anatase, while the arrangements of [TiO_6] units in rutile and brookite result from different combinations of corner sharing and edge sharing.\(^3\) Corner sharing among octahedra is predominant in rutile, which has consequences for the conditions required for selective synthesis of the rutile phase, as will be discussed in Chapter 2. The degree of distortion in the [TiO_6] octahedra differs slightly among the crystal structures: for example, the respective apical and equatorial Ti—O bond lengths are 1.98 and 1.95 Å in bulk rutile, and 1.98 and 1.93 Å in bulk anatase.\(^3\)

At the bulk scale, rutile is the thermodynamically stable phase, while anatase and brookite are metastable. However, as has been recently determined both in atomistic simulations and in calorimetric experiments, the thermodynamic phase stability of TiO_2 is size dependent: although rutile is the stable phase for grain sizes larger than 35 nm, brookite becomes thermodynamically favorable in the size range 11 – 35 nm while anatase is the stable polymorph at grain sizes below 11 nm.\(^6\) The reason for this observed size dependence is that although the interior of a rutile crystal (i.e., the bulk crystal structure) is more energetically stable than that of either of the other two phases, the calculated average surface enthalpy of rutile (1.93 J m\(^{-2}\)) is actually higher than that of
brookite (1.66 J m⁻²) or anatase (1.34 J m⁻²).⁶,⁷ Thus at the nanometer scale, where a crystal’s surface energy begins to dominate the total energy of formation, it becomes more energetically costly to form the rutile phase and one of the other two phases is favored depending on the exact grain size. This is why it is far easier to produce nanoscale anatase under mild conditions than it is to make comparably sized rutile crystals; in particular, the preparation of nanosized rutile by hydrolytic solution-phase routes invariably requires an extremely acidic medium (pH < 1), while nanosized anatase can readily be prepared at neutral or near-neutral pH.

1.2. Important properties of TiO₂

TiO₂ possesses several advantageous physical and chemical properties that have made it one of the most versatile and widely used metal oxides for industrial, environmental, and everyday purposes. It is easy to produce in large quantities, chemically stable, and, at least at the bulk scale, non-toxic. (As is the case with most nanomaterials, the toxicological effects of nanocrystalline TiO₂ are currently unknown and may differ substantially from those of its bulk counterpart; studies are currently being done to determine whether this is the case.)

One property of TiO₂ that makes it especially well suited to photocatalysis and similar applications is its ability to generate OH⁺ radicals that serve as powerful oxidants. These radicals are formed from hydroxyl (OH⁻) groups on the surfaces of TiO₂ particles and are considered one of the most important species in photocatalytic oxidation reactions; their role will be described in more detail in Chapters 4 and 5.
Perhaps most important from an application standpoint is that all three major polymorphs of TiO$_2$ behave as semiconductors, i.e., their electrons occupy bands rather than discrete energy states and they possess an electrical conductivity that increases with increasing temperature. This property, coupled with the previously discussed characteristics, makes TiO$_2$ an ideal material for photovoltaic applications. A semiconductor is characterized by a lower (valence) band, or VB, and an upper (conduction) band, or CB, separated by a “band gap” of energy $E_g$. When the temperature is absolute zero ($T = 0$ K), the electrons in the material all occupy the VB; as the temperature increases, however, the mobility of the electrons increases, and if sufficient thermal energy is added a VB electron may be excited across the band gap into the CB. Alternatively, the excitation energy may come from a light source. In either case, the excitation energy must be greater than the band gap energy $E_g$ for electron promotion to occur.$^8$

The band gap energies of bulk rutile (3.0 eV, $4.8 \times 10^{-19}$ J) and bulk anatase (3.2 eV, $5.1 \times 10^{-19}$ J) have been known for some time, but it was only recently that a value of $E_g$ for bulk brookite was experimentally measured (3.4 eV, $5.4 \times 10^{-19}$ J).$^9$ In the case of photoexcitation, these band gap energies correspond to maximum excitation wavelengths of 410, 385, and 365 nm for rutile, anatase, and brookite respectively. It should be stressed, however, that these values are size dependent; as the size of an individual TiO$_2$ crystal decreases below ~10 nm, the confinement of electrons to a very small volume results in size quantization effects, one of which is that the band gap energy increases; consequently, the electrical conductivity of nanoscale TiO$_2$ is expected to be slightly lower than that of bulk TiO$_2$. A more complete discussion of this phenomenon, especially
as it pertains to the photocatalytic activity of nanocrystalline titania, is included in Chapter 4.

1.3. Applications of TiO$_2$

Historically, TiO$_2$ has been used most often as a white pigment. The polymorph most commonly used for this purpose has been rutile, largely because it is the phase with the highest natural abundance. However, with the advent of semiconducting devices as well as nanotechnology, both the number of applications for TiO$_2$ and the importance attached to the anatase phase in these applications have increased dramatically. In 1972 it was discovered that rutile electrodes could be used for the photoelectrochemical splitting of water to produce hydrogen,$^{10}$ and since that time there have been countless studies devoted to the potential uses and optimization of both anatase- and rutile-based photocatalysts. Ironically, it is anatase that has generally proven to be the better photocatalyst of the two polymorphs.$^{11-13}$ The semiconducting properties of TiO$_2$ are also well suited to such purposes as gas sensing,$^{14}$ energy production with solar cells,$^{15,16}$ and low-temperature oxidation of carbon monoxide (CO); in the last case, an Au/TiO$_2$ hybrid catalyst is used.$^{17,18}$

Although bulk rutile and anatase are central in many of the aforementioned photovoltaic and catalytic applications, their nanoscale counterparts have frequently proven to be superior materials for such purposes. This is especially true when the application in question relies on the adsorption (i.e., physical or chemical adhesion) of atoms or molecules to the TiO$_2$ surface. The reason for this is that a very large percentage of the atoms in any nanomaterial occupy surface sites, i.e., the surface area per gram of
material is larger for smaller particle sizes. As a result, the number of surface sites available for adsorption increases as the size of individual particles decreases, so that the adsorptive capacity is greater for a given mass of nanoscale TiO$_2$ than for the same mass of bulk TiO$_2$. To be sure, the increase in band gap energy in nano-TiO$_2$ relative to the bulk tends to slightly reduce the material’s efficacy as an electrical conductor, but this effect is offset by the benefits of increased adsorptive capacity resulting from the large surface area of the nanomaterial. The implications of size-related effects for the use of TiO$_2$ as a photocatalyst will be elaborated upon in Chapter 4.

1.4. Summary

The major crystalline phases of titanium dioxide have been briefly described and their physical properties discussed, with an emphasis on semiconducting and adsorptive capabilities. The various applications for TiO$_2$ have been enumerated, along with the advantages of using nanoscale TiO$_2$ for applications involving adsorption of atoms or molecules to the surface of the material.

References


4. [http://ruby.colorado.edu/~smyth/min/tio2.html](http://ruby.colorado.edu/~smyth/min/tio2.html).


Chapter 2

Literature review I: Synthesis of titanium dioxide nanocrystals

2.1. Introduction

The synthesis of nanoscale titanium dioxide has been the subject of extensive research over the last two decades. A variety of methods have been developed to prepare TiO₂ nanocrystals with different grain sizes, morphologies, crystalline phases, and surface chemistries. Generally, the synthetic routes to nano-TiO₂, most of which call for titanium (IV) halides and/or alkoxides as the starting materials, can be divided into three categories: (1) aerosol pyrolysis,¹-³⁷ (2) non-hydrolytic solution-phase reactions,³⁸-⁴⁴ and (3) hydrolytic solution-phase reactions.⁴⁵-¹¹² The selection of a particular synthetic strategy depends on what properties are most desirable for the intended application of the product; for instance, aerosol methods are well suited to the preparation of TiO₂ thin films for photovoltaic and catalytic applications,³-⁸,¹⁵,¹⁷,²⁰-²³,²⁵,³⁰,³²-³⁴,³⁶,³⁷ while hydrothermal crystallization methods readily produce ultrafine (grain size < 10 nm) anatase crystallites with high specific surface area (i.e., surface area per gram), a property that is essential for photocatalytic reactions in aqueous suspensions.⁵⁴,⁶⁸,⁸²

This chapter provides an overview of the three classes of nano-TiO₂ syntheses, the typical properties of the materials they produce, and the advantages and disadvantages of each synthetic strategy. At the end of the chapter, this assessment of the different synthetic routes is briefly summarized and is used to explain the choice of methods used to prepare nanocrystalline titania for photocatalytic studies in the present work.
2.2. Aerosol pyrolysis

Preparation of TiO₂ from reactants in aerosol form requires thermal or laser-induced pyrolysis of a titanium-containing precursor, usually either TiCl₄ or a titanium alkoxide (Ti(OR)₄), at temperatures between 200 and 1000 °C. In the case of TiCl₄ precursor, it is necessary to conduct the reaction in the presence of either oxygen gas or water vapor so that oxygen atoms are available to form TiO₂. The oxygen atoms may be present in either molecular (O₂, H₂O) or radical (O⁺, OH⁺) species. The (non-stoichiometric) chemical reaction is then

\[ \text{TiCl}_4 + (\text{O}_2, \text{O}^+, \text{H}_2\text{O}, \text{or} \text{OH}^+) + (\text{flame or laser}) \rightarrow \text{TiO}_2 + (\text{Cl}_2 \text{ or HCl}) \]

(2.1)

On the other hand, when an alkoxide is used as the precursor, it is possible to obtain TiO₂ even when the reaction is carried out in a dry atmosphere such as N₂, since the alkoxy groups in the precursor already contain oxygen atoms:

\[ \text{Ti(OR)}_4 + (\text{flame or laser}) \rightarrow \text{TiO}_2 + \text{organics} \]

(2.2)

An example of a pyrolytic reaction apparatus, based on the setup described by Ahonen et al., is schematically illustrated in Figure 2.1. In a typical pyrolytic reaction, an ultrasonic aerosol generator is used to form droplets of the precursor, which are then taken up by a carrier gas and transported into a quartz reactor tube surrounded by a
Figure 2.1. Schematic diagram of an apparatus for aerosol pyrolysis. The setup shown here is a simplified version of the one illustrated in Ahonen et al., *Journal of Materials Research* 1999, **14**, 3938.

![Schematic diagram of aerosol pyrolysis apparatus](image)

The furnace set to the desired reaction temperature. After TiO₂ particles are produced inside the furnace by pyrolytic oxidation of the precursor, they are collected by electrostatic precipitation, in which a positively charged plate is used to attract the negatively charged particles.¹¹³

As a synthetic strategy, pyrolysis offers four major practical advantages. First, it is environmentally friendly, producing significantly smaller amounts of waste and potentially harmful by-products than most wet chemical methods.²⁹ Secondly, pyrolytic routes to nano-TiO₂ generally produce high-purity materials¹⁹ whose grain sizes, surface areas, and phase compositions (i.e., relative amounts of rutile and anatase) can be tuned.
through selection of an appropriate temperature,\textsuperscript{9,12,15} aerosol flow rate,\textsuperscript{9,29} precursor concentration,\textsuperscript{11} and carrier gas and feed stream for the reactants.\textsuperscript{11,19} For example, Oh and Park\textsuperscript{29} found that both the rutile content and average particle size of TiO\textsubscript{2} powder produced by gas-phase oxidation of TiCl\textsubscript{4} could be increased simply by increasing the flow rate of the carrier gas, while Rulison et al.\textsuperscript{11} determined that average particle size could be increased or decreased by respectively raising or lowering the precursor concentration. Third, many pyrolytic reactions can be performed using simple and inexpensive equipment.\textsuperscript{13,22,33,36} Lastly, pyrolytic methods are advantageous because they often yield crystalline TiO\textsubscript{2} nanoparticles in a single-step reaction. This is not always the case, however; Ahonen et al.\textsuperscript{19} found, for instance, that pyrolysis of titanium (IV) \textit{n}-butoxide in air produced amorphous powders that required subsequent thermal treatment for conversion to crystalline material.

Despite the advantages of pyrolytic methods, this class of syntheses has one significant drawback: the products usually consist of highly aggregated particles with grain sizes larger than 15 nm, both of which characteristics are undesirable when one wishes to produce high-surface area nanocrystals for applications such as catalysis (specific surface areas of powders obtained by aerosol pyrolysis tend to range from 10 to 50 m\textsuperscript{2} g\textsuperscript{-1}). Recently, though, Sun et al.\textsuperscript{31} found that it is possible to produce anatase thin films with grain sizes as low as 7.4 nm by taking advantage of metal organic chemical vapor deposition (MOCVD) technology, which involves oxidation of titanium (IV) alkoxide vapor by pure O\textsubscript{2} gas in a heated quartz tube. The investigators found that anatase nucleation dominated over grain growth at low MOCVD reaction temperatures, and that the optimal temperature for grain size minimization was approximately 700 °C.
Nevertheless, MOCVD technology is largely limited to the production of thin films, and other methods are required for preparation of titania powders with properties comparable to those obtained by Sun et al.

2.3. Non-hydrolytic solution-phase reactions

In order to obtain ultrafine (D < 10 nm) titania powders with correspondingly high surface area, one usually must resort to wet chemical methods. Although these syntheses usually involve hydrolytic reactions that require an aqueous environment, researchers have recently developed ways to produce nanocrystalline TiO₂ in the absence of water.⁴⁸-⁴⁴ Such nonhydrolytic routes involve elimination reactions at mildly elevated temperatures (80 – 300 °C) between a titanium (IV) halide (usually TiCl₄) and an oxygen donor that can be a titanium (IV) alkoxide, an ether, or an alcohol.⁴⁸,⁴⁹,⁴² The overall reactions for these three routes, known respectively as condensation, etherolysis, and alcoholysis, are listed below:⁴²

\[
\text{TiX}_4 + \text{Ti(OR)}_4 \rightarrow 2 \text{TiO}_2 + 4 \text{RX} \quad \text{(condensation)} \\
\text{TiX}_4 + 2 \text{ROR} \rightarrow \text{TiO}_2 + 4 \text{RX} \quad \text{(etherolysis)} \\
\text{TiX}_4 + 2 \text{ROH} \rightarrow \text{TiO}_2 + 2 \text{RX} + 2 \text{HX} \quad \text{(alcoholysis)}
\]

Despite the apparent simplicity of these reactions, their mechanisms usually involve multiple steps. For instance, in the case of etherolysis and alcoholysis, the ether and alcohol molecules first react with the halide groups of some of the precursor molecules to
create Ti—OR functionalities in a process called alkoxylation, after which the alkoxide groups react with remaining titanium halide molecules to form Ti—O—Ti linkages: \[ \equiv \text{Ti}—X + \equiv \text{R—OR} \rightarrow \equiv \text{Ti—OR} + \equiv \text{R—X} \] (2.6a) \[ \equiv \text{Ti—X} + \equiv \text{Ti—OR} \rightarrow \equiv \text{Ti—O—Ti═} + \equiv \text{R—X} \] (2.6b)

Furthermore, the Vioux research group\(^{38,39,42}\) has noted that reactions (2.3) through (2.5) are only facile when the temperature is elevated above about 80°C; at room temperature, the formation of TiO₂ in a nonhydrolytic reaction is very slow, and in fact the primary reaction between the precursor molecules is a ligand-exchange process (also known as redistribution) that results in titanium haloalkoxides:

\[ \equiv \text{Ti—X} + \equiv \text{Ti’—OR} \rightarrow \equiv \text{Ti—OR} + \equiv \text{Ti’—X} \] (2.7) \[ \equiv \text{Ti—X} + \text{R—OR} \rightarrow \equiv \text{Ti—OR} + \equiv \text{R—X} \] (2.8) \[ \equiv \text{Ti—X} + \text{H—OR} \rightarrow \equiv \text{Ti—OR} + \equiv \text{H—X} \] (2.9)

Because of the above mechanistic considerations, then, one can expect nonhydrolytic titania syntheses to be quite sensitive to such reaction parameters as precursor concentration, choice of halide and alkoxy substituents, the temperature at which the reactants are mixed, and, in the case of reactions (2.4) and (2.5), selection of a particular ether or alcohol. This sensitivity allows one to exert considerable control over the properties of the materials obtained from a nonhydrolytic reaction. Arnal et al.\(^{38}\) found that anatase, rutile, and mixed rutile-brookite nanocrystals could be formed via the
reaction of TiCl₄ at 110 °C with diethyl ether, ethanol, and t-butyl alcohol respectively. More recently, Trentler et al.⁴¹ determined that the reaction between titanium (IV) isopropoxide (Ti(ÔPr)₄) and various titanium (IV) halides in heptadecane solvent yielded anatase particles whose grain sizes decreased both with increasing size of the halide substituent and with the inclusion of trioctylphosphine oxide (TOPO) as a surfactant. TOPO was also found to favor phase-pure products, whereas halide-alkoxide condensation reactions in the absence of TOPO yielded mixtures of anatase, rutile, and brookite.

Clearly, the tunable grain sizes and degree of phase control offered by nonhydrolytic routes make this class of reactions attractive as a synthetic strategy for engineered nanomaterials. Additionally, nonhydrolytic syntheses are advantageous because they often require very short (~ 5 min.) reaction times, occur under mild thermal conditions (80 – 300 °C), and tend to produce very fine grains (4 – 10 nm) with minimal aggregation of primary particles.⁴¹

The main disadvantages of these reactions are that they necessarily demand the maintenance of a dry atmosphere to prevent hydrolytic side reactions and that, in some cases, the as-prepared TiO₂ powders require subsequent heat treatment in order to obtain crystalline material.³⁸ Also, while the use of a surfactant such as TOPO may ensure both phase purity and ultrafine grains, it also results in products with surfaces covered with organic ligands that are difficult to remove.

Perhaps the most unique feature of nonhydrolytic reactions is their ability to produce nano-TiO₂ particles whose surfaces are completely dehydroxylated, owing to the absence of water during the synthesis. This dehydroxylation can be either an advantage or
a liability, depending on the application of the material; for example, the absence of
surface hydroxyls is beneficial when one wishes to maximize the reducing power of a
titania surface,\textsuperscript{41,114} but in applications such as photocatalysis it is essential to have
hydroxylated surfaces in order to produce the OH$^*$ radicals that are thought to be the
active species in oxidative decomposition of adsorbed contaminants.\textsuperscript{115}

\section*{2.4. Hydrolytic solution-phase reactions}

To generate hydroxylated materials while retaining the desirable properties
afforded by nonhydrolytic synthesis, it is necessary to turn to the other class of wet
chemical methods: hydrolytic solution-phase processes. Such routes represent the most
common laboratory strategy for obtaining both bulk and nanoscale TiO\textsubscript{2}. In these
reactions, a titanium-containing precursor (usually a titanium (IV) halide, titanium (IV)
alkoxide, or titanyl sulfate) reacts with water and forms Ti—O—Ti bridges to create solid
TiO\textsubscript{2}:

\begin{align*}
\text{TiX}_4 + 2 \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4 \text{HX} \quad (2.10) \\
\text{Ti(OR)}_4 + 2 \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4 \text{ROH} \quad (2.11) \\
\text{Ti(SO}_4)_{2} + 2 \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 2 \text{H}_2\text{SO}_4 \quad (2.12)
\end{align*}

In these reactions, water is often used as the solvent or is at least present in vast excess;
however, it is also possible to react the precursor with a stoichiometric amount of water
in an alcohol or other solvent if one wishes to perform a more controlled hydrolysis.
If hydrolytic reactions are carried out under ambient conditions and in the absence of any other reagents, the resulting titania powder will be amorphous. To ensure a crystalline product, hydrolysis must be accompanied or followed by one or more of the following processes: (1) calcination,\textsuperscript{53,59,78,89,110} (2) refluxing in the presence of an acid or a surfactant that forces the Ti—O—Ti linkages to adopt a crystalline structure,\textsuperscript{46,48,51,56,58,60,64,80,86-88,97-100,103,104,108,111,112} or (3) hydrothermal treatment.\textsuperscript{45,47,49,52,54-58,66-77,79-82,85-88,90,92,93,96-100,102-104,106,107,109} As will be seen shortly, only the second and third processes are viable strategies for producing very small grain sizes; nevertheless, because of the degree of phase control offered by the calcination method, it is included here as a relevant synthetic route to nanomaterials with tunable properties. Each of these crystallization strategies is discussed and evaluated below.

2.4.1. Hydrolysis followed by calcination.

The first way to obtain crystalline titania from a hydrolytic reaction is to first form amorphous titania using any of the reactions (2.10) through (2.12) and then calcine the amorphous material, i.e., heat it at ambient pressure in the presence of oxygen. One can, to a limited extent, control the grain size of the crystalline product by selecting a low or high calcination temperature; generally, coarser grains are obtained at higher temperatures.\textsuperscript{89} Depending on the hydrolysis conditions, crystallization of amorphous TiO\textsubscript{2} to the anatase phase occurs at calcination temperatures between 250 and 400 °C. Transformation from anatase to rutile takes place at higher temperatures, usually over the range 500 – 1000 °C; again, the exact transformation temperature depends on the conditions under which the amorphous material was originally prepared. Above 500 °C,
an increasing amount of rutile is observed with increasing temperature, indicating that the anatase-to-rutile transition takes place gradually.53,59 Because this phase transformation occurs over a range of temperatures, by varying the heating time and temperature one can obtain anatase-rutile mixtures with tunable compositions. The ability to control phase composition has recently proven useful in the optimization of photocatalytic activity of mixed-phase titania.116

Although calcination is appealing as a simple, facile means of obtaining crystalline titania, it is, as mentioned before, decidedly ill-suited to the production of ultrafine (D < 10 nm) nanocrystals. Because heating invariably leads to grain growth, it is difficult to obtain fine-grained anatase and practically impossible to obtain fine-grained rutile by heating an amorphous sample. As is the case with aerosol pyrolysis, calcination seldom produces nanocrystals smaller than 15 – 20 nm, and the particles are usually severely aggregated or agglomerated, which further reduces their specific surface area.

2.4.2. Hydrolysis with acids or surfactants

One alternative to calcination that yields finer, less aggregated nanocrystals is the hydrolysis of a titanium-containing precursor followed by refluxing in the presence of a strong acid (usually either HNO₃ or HCl) or surfactant at temperatures between 60 and 100 °C. Acids and surfactants not only catalyze the formation of crystalline TiO₂ structures but also act as peptizing agents, i.e., reagents that stabilize individual nanocrystal surfaces, thus preventing aggregation, discouraging particle growth, and allowing the particles to exist in the form of a colloidal sol.
2.4.2.1. Acid reflux

The acid reflux method is an attractive option for hydrolytic TiO₂ synthesis because it is straightforward and often yields remarkably fine, monodisperse nanoparticles ranging from 2 to 10 nm in size.¹⁴⁻¹⁴,¹⁸,⁶⁰,⁹¹,¹¹¹ The crystalline phase of the products obtained in such reactions depends primarily on the concentration of acid. Generally speaking, wet chemical formation of rutile nanocrystals requires a highly acidic environment (pH << 1). The reason for this observation becomes apparent upon consideration of the crystal structures of anatase and rutile; the former consists of edge sharing [TiO₆] octahedral units, while the latter consists primarily of corner sharing octahedra with a smaller degree of edge sharing. In aqueous solution, Ti(IV) (3d⁰) ions exist in the form of octahedrally coordinated complexes, in which at least some of the ligands are either water (H₂O) molecules or hydroxyl (OH⁻) groups. Solid TiO₂ forms as a result of condensation reactions among these Ti(IV) (3d⁰) coordination complexes, i.e., reactions between OH⁻ ligands on different complexes resulting in the elimination of water to form Ti—O—Ti linkages. As Figure 2.2 shows, if the number of OH⁻ ligands in the coordination complexes is large there is a greater probability of edge shared bonding (and thus anatase formation) among [TiO₆] octahedra when TiO₂ forms, while corner shared bonding (and thus rutile formation) is favored when the number of OH⁻ ligands is small. Because relatively few OH⁻ ligands are present under acidic conditions, it follows that addition of a strong acid to a hydrolytic reaction system should encourage the formation of the rutile phase and suppress the formation of the anatase phase. The higher the acid concentration, the more strongly rutile is favored. Correspondingly, if the pH of the medium is neutral or basic,
Figure 2.2. Influence of OH⁻ ligands on the crystallization of TiO₂ from hydrolytic reactions. Acidic conditions, under which the number of OH⁻ ligands is small, tend to favor the corner sharing among [TiO₆] octahedra that is characteristic of the rutile structure, while the increased number of OH⁻ ligands under neutral to basic conditions favors the edge-shared bonding characteristic of anatase. Ligands other than OH⁻ are simply denoted L. (See also Cheng et al., Chemistry of Materials 1995, 7, 663.)

Acidic conditions, low number of OH⁻ ligands

Corner-shared bonding, rutile favored

Neutral to basic conditions, high number of OH⁻ ligands

Edge-shared bonding, anatase favored
then anatase is the favored product. In both cases, a small amount of brookite impurity is also observed.\textsuperscript{52}

The properties of nano-titania obtained by acid reflux also depend on the choice and concentration of acid as well as on the reaction temperature. Watson et al.,\textsuperscript{111} for instance, observed a dependence of the crystalline phase, grain size, and morphology on the reaction temperature when titanium (IV) isopropoxide was refluxed in 0.56 M HNO\textsubscript{3}; at lower temperatures (60 °C) needle-like rutile particles with lower surface area (95 m\textsuperscript{2} g\textsuperscript{-1}) were observed, while at higher temperatures (90 °C) the product consisted of agglomerates of anatase dots and had a remarkably high specific surface area (299 m\textsuperscript{2} g\textsuperscript{-1}). The results of Bischoff and Anderson\textsuperscript{51} qualitatively corroborate the temperature dependence of crystalline phase; they found that peptization of amorphous titania with 0.1-0.5 M HNO\textsubscript{3} at room temperature yielded a mixture of rutile (D = 12.2 nm) and anatase (5.3 nm), while refluxing the acid-titania system at higher temperatures resulted in formation of the anatase phase (5.3 – 6.5 nm) with a trace amount of brookite; in both cases the specific surface areas were quite high (150 – 250 m\textsuperscript{2} g\textsuperscript{-1}). On the other hand, Bischoff and Anderson noted that in addition to this temperature dependence, the properties of the product were influenced by the choice of acid; when the amorphous titania was refluxed in the presence of 0.5 M H\textsubscript{2}SO\textsubscript{4}, the product was 4.9 nm anatase with a strikingly low surface area (10 m\textsuperscript{2} g\textsuperscript{-1}), a result Bischoff and Anderson attributed to the tendency of the sulfate ion to complex strongly with titanium ions and encourage the growth of anatase particles so that the porosity of the final product was greatly reduced.

More recently, Huang and Gao\textsuperscript{108} showed that a simple acid reflux could be used to obtain phase-pure rutile with anisotropic morphologies; specifically, they found that by
refluxing a TiCl₄ aqueous solution in concentrated (15 M) HNO₃ they could produce rutile nanorods with diameters of 4 – 6 nm and lengths of 50 – 150 nm. Thus acid reflux not only offers control over crystalline phase and particle size but also provides a means of synthesizing particles with different shapes that could potentially exhibit interesting optical, magnetic, and electronic behavior.¹⁰⁸

Because of its simplicity and the amount of control it offers over nanocrystal properties, acid reflux is one of the better methods for making nanocrystalline titania. Its chief disadvantage is that it is time-consuming; Gribb and Banfield, for instance, report a method that requires not only a 72 h reflux but also a subsequent aging period of approximately three weeks in order to convert the gel obtained during reflux into a dried, usable anatase powder.⁶⁰ To be sure, some acid-reflux protocols require considerably shorter aging times, as Watson et al. demonstrated with their HNO₃ reflux which lasted only 1 h.¹¹¹ Even in such cases, however, it is necessary to repeatedly wash the nanocrystalline product and/or dialyze against water before the particles can be used for various applications (see also Section 2.4.2.2); such post-synthetic processing adds a considerable amount of time to the preparation of nano-TiO₂ powders.

2.4.2.2. Surfactant-based methods

Like acids, surfactants serve a threefold purpose: they promote the formation of crystalline titania, ensure small particle sizes, and stabilize individual crystallites against aggregation. One surfactant-based method, developed in 1998 by Scolan and Sanchez,⁶⁴ involves room-temperature hydrolysis of titanium (IV) n-butoxide in n-butanol solvent in the presence of para-toluenesulfonic acid (PTSH) and acetylacetone, followed by aging at
60 °C. This synthesis yields very small, monodisperse, non-aggregated anatase crystallites with sizes ranging from 1 to 5 nm depending on the exact reaction conditions. The authors proposed that the combination of acetylacetonato complexing ligands at the particles surfaces and PTSH-based species located in a solvating layer around the particles ensures the surface protection necessary for small particle sizes while simultaneously allowing for the necessary rearrangement of oxo-polymers and metal oxo-clusters to form anatase crystals.

A particularly popular class of surfactants used in nano-titania synthesis comprises the tetraalkylammonium hydroxides (general formula NR$_4^+$OH$^-$. It should be noted that because these compounds are basic, their use in hydrolytic preparation of TiO$_2$ virtually guarantees exclusive formation of the anatase phase. The OH$^-$. ion catalyzes the hydrolytic reaction that forms anatase, while the NR$_4^+$ ions associate with the negatively charged TiO$_2$ nanoparticle surfaces thus forming a stable sol.$^{67,79,86,87}$ Recently Chemseddine and Moritz$^{67}$ developed a wet chemical synthesis of nanocrystalline anatase in which simple variations in the concentration of tetramethylammonium hydroxide (TMAH) surfactant afford excellent control over not only particle size but also morphology and organization of titania crystallites. Their method is a straightforward, two-step procedure consisting of low-temperature precipitation of amorphous titania from an alkoxide precursor in a dilute aqueous TMAH solution followed by refluxing under inert gas for 6 h. The results of Chemseddine’s and Moritz’s 1999 paper indicated that the tetramethylammonium cation (N(CH$_3$)$_4^+$) associates preferentially with the (1 0 1) face of anatase, thus discouraging addition of new structural units to the (1 0 1) surfaces during crystal growth (Figure 2.3). The result of this preferential cationic association is that the
Figure 2.3. Effect of tetramethylammonium cations (N(CH₃)₄⁺) on anatase nanocrystal growth. The N(CH₃)₄⁺ ions associate preferentially with the anatase (1 0 1) faces, resulting in anisotropic growth that yields rodlike particles in which (1 0 1) surfaces are predominant. (Illustration courtesy of Chemseddine and Moritz, *European Journal of Inorganic Chemistry* 1999, **1999**, 235.)

anatase crystals grow anisotropically – specifically, particle growth initially proceeds rapidly in the [0 0 1] direction, followed by branching in the [0 1 0] and [1 0 0] directions – so that at the end of the reaction the particles will be dominated by (1 0 1) surfaces.

In addition to achieving morphological control by adding tetraalkylammonium reagents at different concentrations, one can readily tune the size of hydrolytically derived TiO₂ nanocrystals by changing the size of the alkyl substituents of the tetraalkylammonium cation. Yang et al.⁸⁶,⁸⁷ studied nano-anatase synthesis in the presence of tetramethyl-, tetraethyl-, and tetrabutylammonium hydroxide and found that increasing the size of the alkyl group from one to four carbons had the effect of decreasing the average anatase grain size from 41 to 20 nm. The authors proposed two possible explanations for this trend. In one suggestion, the tetraalkylammonium cations with larger alkyl substituents were more effective in preventing collisions among anatase
primary particles and thus in preventing growth. In the other suggested explanation, the weaker basicity of the tetraalkylammonium hydroxide with larger alkyl groups reduced the likelihood of an OH⁻ ligand being donated to a Ti(IV) d⁰ complex ion in solution, which in turn would reduce the likelihood of condensation reactions between such complexes to create Ti—O—Ti linkages and form solid TiO₂. Either way, it was clear that one could easily control particle size by choosing an alkyl substituent that suppresses particle growth to a greater or lesser extent.

Some investigators employ multiple surfactants in synthesizing nano-titania; in such cases one surfactant may act as a catalyst for the formation of crystalline material while another serves to stabilize the particles against aggregation. For example, Kotov et al.⁵⁰ prepared stable dispersions of titania nanoparticles by hydrolyzing titanium (IV) isopropoxide in the presence of both cetyltrimethylammonium bromide (CTAB) and tetramethylammonium hydroxide (TMAH), where CTAB was the surface stabilizing agent and TMAH functioned as the catalyst. The particles obtained from this two-surfactant preparation were among the smallest reported in the literature, with diameters between 1.8 and 2.2 nm. However, it is unclear from the authors’ publication whether the product consisted entirely of anatase or contained a small amount of some other phase.

As illustrated by the above examples, the surface-stabilizing properties of the reagents used in surfactant-based reactions make this class of hydrolytic syntheses ideal for the preparation of very fine nanocrystals (2 – 10 nm) in the form of stable colloids. Yet despite the extremely high specific surface areas of such small particles, the surfaces are of little practical use for applications such as catalysis that require empty surface sites for adsorption. In colloidal sols, the titania particles’ surfaces are already covered with
surfactant molecules, which precludes the adsorption of other species to active surface sites and thus prevents catalytic reactions from occurring to any appreciable extent. If one wishes to use the titania for catalysis or some other application requiring that surface sites be available, one must first remove the surfactant from the particle surfaces by a combination of salting out, washing, centrifugation, and dialysis, all of which are labor-intensive and time-consuming. An additional disadvantage to surfactant-based methods is the amount of hazardous aqueous waste they generate, particularly when one considers the relatively small amount of product yielded in such reactions; the method of Chemseddine and Moritz, for instance, yields only about 100 mg of solid TiO₂ per 150 mL of aqueous TMAH.⁶⁷

2.4.3. Hydrothermal synthesis

The most popular technique in hydrolytic preparation of nanocrystalline titania is hydrothermal processing, i.e., crystallization at elevated temperature and pressure in the presence of water. Properly speaking, this technique is termed “solvothermal” (or, alternatively, “solvatothermal”) processing when a liquid other than water is used as the solvent, even if water is present for hydrolysis.¹¹⁷ However, many researchers use the terms “hydrothermal” and “solvothermal” interchangeably, and in the present work the word “hydrothermal” will be used to describe any high-temperature, high-pressure solution-phase reaction regardless of whether the solution is aqueous or non-aqueous.

Hydrothermal crystallization is carried out in a sealed autoclave, or “bomb” reactor, an example of which is shown in Figure 2.4. Bomb reactors are usually made of stainless steel or titanium, though it is possible to purchase vessels made from corrosion-
resistant alloys that allow one to perform reactions under highly acidic or basic conditions. If the autoclave material is not corrosion-resistant, a Teflon liner may be used to protect the vessel’s interior during reactions that call for corrosive solvents. However, because Teflon melts around 250 ℃, it cannot be used in reactions above that temperature.

In a hydrothermal reaction, a heating mantle or oven is used to raise the temperature above the standard boiling point of the solvent, at which point the evaporating solvent begins to generate a pressure inside the sealed vessel; this pressure,
due exclusively to the refluxing solvent, is known as “autogenous” pressure. The
temperature required for crystallization of TiO₂ under hydrothermal conditions depends
on the material; in the case of titania, typical reaction temperatures reported in the
literature range from 150 to 350 °C, significantly below the temperatures needed for
crystallization via calcination (see Section 2.4.1). Hydrothermal reaction times are often
as short as 2 h and are rarely longer than 1 – 2 days.

Hydrothermal processing of either amorphous titania or a titanium-containing
precursor has been shown to be an ideal method for obtaining titania with small grain
sizes (often 10 nm or less), high specific surface areas (150-280 m² g⁻¹), and high
crystallinity. ⁴⁵,⁴⁷,⁴⁹,⁵²,⁵⁴-⁵⁸,⁶⁶-⁷⁷,⁷⁹-⁸²,⁸⁵-⁸⁸,⁹⁰,⁹₂,⁹³,⁹⁶-¹⁰⁰,¹⁰²-¹⁰⁴,¹⁰⁶,¹⁰⁷,¹⁰⁹ Usually hydrothermal
crystallization is performed on a suspension or slurry of amorphous titania obtained from
hydrolysis of TiCl₄ or a titanium (IV) alkoxide. However, in some cases investigators
combine the hydrolysis and crystallization steps in a single-vessel process. This can be
accomplished either by injecting a solution of the precursor into a pre-heated bomb or by
initially placing the precursor (dissolved in an organic solvent) and the hydrolysis water
in separate regions of the bomb so that they only come in physical contact when the water
boils upon heating of the reaction mixture. The latter strategy of performing controlled
hydrolysis with a limited amount of water in an organic solvent – a method developed by
Kominami, Ohtani, et al. and dubbed HyCOM (Hydrothermal Crystallization in Organic
Media) – tends to produce powders consisting of very fine crystallites of anatase (10 – 30
nm) with high surface areas (50 – 280 m² g⁻¹) and, correspondingly, good photocatalytic
performance owing the presence of a large number of surface sites for
adsorption. ⁵⁴,⁵⁵,⁵⁷,⁶⁸,⁶⁹,⁷⁶,¹⁰⁹ The authors attributed the formation of such fine particles to
the low solubility of TiO$_2$ in organic solvents, the consequence of which is that anatase nanocrystals, once nucleated, are unlikely to grow to an appreciable extent via dissolution and reprecipitation of TiO$_2$ (a phenomenon known as Ostwald ripening). In 1999, taking the strategy of suppressing Ostwald-type growth one step farther, Kominami et al. developed a method that uses water “homogeneously liberated” from an alcohol solvent during heating as the sole source of hydrolysis water, a technique that not only improves the anatase product’s photocatalytic activity but also yields crystallites as small as 11 nm, given the appropriate combination of alcohol solvent and alkoxide precursor.$^{68}$

The importance of the amount of hydrolysis water, and particularly the molar ratio of water to precursor, has been investigated in numerous works yet remains ambiguous due to the great variety of hydrothermal reactions reported in the literature. It has been noted, for instance, that in cases where amorphous titania is prepared from an alkoxide, an increase in the water:alkoxide ratio (also known as the hydrolysis ratio, denoted $r$) correlates with a decrease in grain size in the crystallized product. This is because the higher water content results in a more rapid hydrolysis rate thus favoring nucleation of new particles over growth of existing particles.$^{72,94}$ Yet this correlation between hydrolysis ratio and grain size may not be so simple; recently, Hsu and Nae$^{101}$ reported a synthesis in which a hydrothermal crystallization of anatase in the presence of HNO$_3$ or HCl yielded finer particles when the hydrolysis ratios were low rather than high. The authors explained their results by noting that hydrogen bonding among freshly nucleated anatase particles would be enhanced at higher hydrolysis ratios (i.e., greater water concentrations), thus encouraging the aggregation and eventual coalescence of those anatase nuclei to form coarser primary particles. Nevertheless, it is clear from the
existing literature that under a given set of conditions, one can change the properties of TiO₂ nanocrystals by manipulating the hydrolysis ratio, provided one has a reasonable understanding of the other reaction parameters that influence the physical characteristics of the product.

As is the case with other hydrolytic methods, one can selectively obtain a particular crystalline phase from a hydrothermal reaction by adjusting the pH of the reaction medium. Acidic conditions favor the rutile phase, whereas neutral to basic conditions tend to produce the anatase phase; in both cases, brookite is sometimes observed as the minor phase (see Section 2.4.2.1 for a more detailed discussion of pH-dependent phase composition). Phase purity also depends on the hydrothermal treatment temperature; the range 210 – 240 °C appears to be optimal for obtaining anatase, whereas rutile and brookite impurities are observed for anatase synthesized outside this temperature range.²⁸,²⁷,²⁸

When hydrothermal synthesis is performed without a surfactant, the primary particles in the product tend to form loose aggregates, but there is usually little (if any) of the severe agglomeration observed in calcined titania samples.¹¹⁸ Despite the advantages that hydrothermal synthesis offers, however, it rarely yields titania with specific surface areas above 200 m² g⁻¹. Occasionally, higher surface areas (200-280 m² g⁻¹) have been reported for nano-anatase in the literature, but in most of these cases the synthetic methods have either required long aging times, involved harmful organic solvents such as toluene, or resulted in small amounts of brookite impurity in the final anatase product.²⁷,²⁹,³⁴,¹⁰⁹
2.4.5. Combined hydrolytic strategies

To effect maximum control over the properties of nanocrystalline titania obtained by hydrolytic preparations, many researchers combine the strategies of hydrothermal treatment and peptization. The former technique, with its combination of high temperature and high pressure, allows one to form crystalline titania in a very short time and in appreciable quantities, while the latter technique of peptization ensures that the particles are extremely small and unagglomerated (even upon removing surfactant molecules by dialysis and/or washing to obtain a powder, one will have loosely aggregated particles rather than hard, fused agglomerates that are difficult or impossible to break up). Between the choice of hydrothermal processing parameters (e.g., temperature and reaction time) and the assortment of chemical variables (e.g., type and amount of peptizing agent, type and amount of precursor, and amount of hydrolysis water), there are almost endless variations on the peptization-hydrothermal processing combination, each of which allows one to exert a different kind and degree of control over one or more properties of the nanocrystalline product. To be sure, the use of certain techniques (e.g., the use of surfactants which must subsequently be removed by dialysis) requires that one sacrifice time or convenience in order to better manipulate particle characteristics, but by combining hydrothermal and peptization techniques it is often possible to strike a good balance between the quality of the product and the ease and efficiency of the synthetic method.
Table 2.1. Summary of synthetic routes to nanocrystalline TiO₂.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction T (°C)</th>
<th>Grain sizes (nm)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>aerosol pyrolysis</td>
<td>200 – 1000</td>
<td>&gt; 15</td>
<td>• environmentally friendly</td>
<td>• large particles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high crystallinity</td>
<td>• aggregation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• tunable phase composition</td>
<td></td>
</tr>
<tr>
<td>non-hydrolytic, solution-phase</td>
<td>80 – 300</td>
<td>4 – 10</td>
<td>• short reaction times</td>
<td>• organic ligands on surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• very fine particles</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• minimal aggregation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high surface area</td>
<td></td>
</tr>
<tr>
<td>hydrolysis + heat treatment</td>
<td>500 – 1000 (calcination)</td>
<td>&gt; 15</td>
<td>• fast, easy synthesis</td>
<td>• large particles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high crystallinity</td>
<td>• severe aggregation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• tunable phase composition</td>
<td></td>
</tr>
<tr>
<td>hydrolysis + peptization (acid or surfactant)</td>
<td>60 – 100</td>
<td>2 – 10</td>
<td>• very fine particles</td>
<td>• surfactant on surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• minimal aggregation</td>
<td>• sometimes produces large amounts of aqueous waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high surface area</td>
<td>• sometimes requires long reaction times</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high crystallinity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• tunable morphologies and phase composition</td>
<td></td>
</tr>
<tr>
<td>hydrolysis + hydrothermal treatment</td>
<td>150 – 350</td>
<td>8 – 30</td>
<td>• very fine particles</td>
<td>• some aggregation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high surface area</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• fast, easy synthesis</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• high crystallinity</td>
<td></td>
</tr>
</tbody>
</table>
2.5. Summary and relevance to present work

The various types of methods for synthesizing nanocrystalline TiO$_2$ are summarized and briefly evaluated in Table 2.1. It should be noted that although "advantages" and "disadvantages" are enumerated for each method, the question of whether a particular characteristic is advantageous often depends primarily on the intended application of the product, as was pointed out at the beginning of the chapter. In the case of the present work, one of the major objectives was to evaluate the effects of multiple physical properties – i.e., grain size, specific surface area, phase composition, and morphology – on the photocatalytic performance of nanocrystalline TiO$_2$ powders, and to determine which physical characteristics were most critical for optimizing photocatalytic efficiency. Because it is already known that large specific surface area and high crystallinity are both critical characteristics of efficient TiO$_2$ catalysts, it was apparent that hydrothermal processing, peptization, or a combination of both would be necessary for the production of powders whose photocatalytic activity could be expected to be reasonably high. As discussed in Section 2.4.5 and as shown in Table 2.1, the hydrothermal method guarantees the formation of highly crystalline materials in a short time, while peptization techniques ensure minimal aggregation, fine particles, and good control over phase composition and particle morphology.

Most of the materials used for the photocatalytic studies in this work could be readily prepared according to previously published methods with only slight modifications: anatase rods of controllable aspect ratio were synthesized using the surfactant-based strategy of Chemseddine and Moritz$^{67}$ along with subsequent hydrothermal treatment, while ultrafine rutile and anatase-rutile mixtures were obtained
using a simplified version of the low-pH reflux described by Cheng et al., in which highly acidic conditions facilitated the formation of rutile-phase TiO₂. The preparation of anatase dots has also been described many times in the literature, but in the interest of developing an improved route to high surface area, ultrafine anatase with tunable properties, a portion of the current work was devoted to preparing such a product using a simple hydrothermal synthesis in ethanol. This anatase synthesis has been submitted for publication and is described in detail in Chapter 3.

References


S. Seifried, M. Winterer, and H. Hahn, *Chemical Vapor Deposition*, 2000, 6, 239.


http://www.eas.asu.edu/~holbert/wise/electrostaticprecip.html, in 'Electrical engineering for pollution control: electrostatic precipitators for power plants'.


Chapter 3

Hydrothermal synthesis and characterization of anatase TiO₂ nanocrystals with ultra-high surface area

3.1. Introduction

This chapter describes a rapid hydrothermal synthesis to produce phase-pure, monodisperse anatase nanocrystals with small grain size and high specific surface area. Such sample characteristics should maximize the performance of nanoscale titania in the many applications that rely on its surface chemistry. The method used in this work involved injection of a precursor solution directly into a pre-heated bomb reactor, a strategy that not only ensures rapid nucleation (and thus smaller particles) but also minimizes the amount of time and equipment required for each reaction. To further promote fine grain sizes and large surface areas, hydrothermal reactions were performed at relatively low temperature (140 – 300 °C) using short reaction times so as to minimize grain growth via Ostwald ripening. Additionally, the reactions were conducted under near-neutral conditions to encourage the exclusive formation of anatase. Finally, to probe the effects of the water:alkoxide molar ratio (also known as the hydrolysis ratio, or \( r = [\text{H}_2\text{O}] / [\text{Ti(OR)}_4] \)), the reactions were run in ethanol solvent rather than water, so that fine adjustments in the amount of hydrolysis water are possible.

This work demonstrated that hydrothermal synthesis of titania in ethanol produces nanocrystalline anatase with grain sizes as small as 5.5 nm and surface areas as high as 250 m² g⁻¹. This synthesis enables one to tune particle sizes by adjusting reaction parameters such as temperature, precursor concentration, and hydrolysis ratio; in
particular, the findings presented here suggest that very small nanocrystals with ultra-high surfaces areas can be obtained using $T = 140 - 150 \degree C$, low concentrations of Ti(OR)$_4$, and hydrolysis ratios ($r = [H_2O] / [Ti(OR)_4]$) between 5 and 15.

3.2. Experimental

3.2.1. Materials for hydrothermal synthesis

The titanium (IV) ethoxide (97%) precursor used in this study was purchased from Avocado Research Chemicals. Ethanol (190 and 200 proof) was from Pharmco Products and ultrapure water was obtained from a MilliQ purification system. Commercial TiO$_2$ samples were generously donated by the Degussa Corporation (P25) and the Tomson Research Group at Rice University (Altair TiNano) for comparison with the homemade TiO$_2$ powders. Hydrothermal reactions were performed in a 450-mL, corrosion resistant Monel pressure vessel (Parr Instruments, Model #4562) equipped with a temperature controller (Parr Instruments, Model #4843) and an automatic cooling loop to maintain the reaction temperature at a constant value. Whatman Type 2 ashless paper circles were used for vacuum filtration of the products. (Note: The equipment used for sample characterization is described in Section 3.2.3.)

3.2.2. Hydrothermal reactions

Hydrothermal titania samples were prepared as follows: first, a known amount of MilliQ water was dissolved in dry ethanol (90 mL) and heated with stirring to the desired reaction temperature inside the Monel pressure vessel. A solution of a predetermined
volume of titanium (IV) ethoxide in dry ethanol (10 mL) was prepared in a flask equipped with a rubber septum to prevent premature hydrolysis of the ethoxide. Once the bomb reached the desired reaction temperature, the precursor solution was transferred to a stainless steel pressure pipette and charged into the reactor. A momentary temperature decrease of 5-10 °C was observed upon injection of the ethoxide solution, but the target reaction temperature was restored within 1-2 min. The reaction mixture was stirred at constant temperature for 2 h and then quenched by plunging the bomb into a room-temperature water bath.

After the autoclave had cooled, the product mixture, which consisted of white TiO$_2$ powder suspended in the ethanol solvent, was transferred to a plastic beaker and agitated for 5-10 minutes in a sonication bath to break up aggregates. The sonicated suspension was then vacuum filtered in order to remove large aggregates from the product. The filtered TiO$_2$ solid was isolated via a 10-30 min. centrifugation at 4200 rpm, washed with either 190-proof ethanol or MilliQ water, and dried either under vacuum or in an 80-90 °C oven.

3.2.3. Characterization

X-ray diffraction (XRD) spectra were taken using a Siemens Platform-Model General Area Detector Diffraction System (GADDS) with a Cu Kα source. The powder samples were run with an internal silicon powder standard in order to account for instrumental line broadening when calculating grain sizes from the anatase linewidths. XRD samples were prepared by thoroughly grinding titania powders with silicon and mounting the resulting mixture on a piece of double-sided tape on the surface of a metal
stub obtained from Electron Microscopy Sciences, Inc. Each powder sample was pressed tightly onto the tape in a continuous, thick, uniform layer to ensure a high-quality spectrum. Each spectrum was taken using a voltage of 50 kV, a current of 40 mA, and a total collection time of 10-60 minutes. Grain sizes were estimated according to the Debye-Scherrer formula with Warren’s correction for instrumental broadening:

\[
D (\text{Å}) = 0.89\lambda / \beta \cos \theta_B
\]  

(3.1)

where \(D\) is the crystallite size, \(\lambda\) is the X-ray wavelength (1.54 Å for Cu Kα radiation), \(\theta_B\) is the Bragg angle, and \(\beta = (B^2 - b^2)^{1/2}\) where \(B\) and \(b\) are taken as the full width at half maximum of, respectively, the anatase [1 0 1] line and the [1 1 1] line of the silicon standard. Because line broadening due to size effects is only significant for very small crystallites (\(D < 20\) nm), grain size determination from XRD linewdths was not feasible for the commercial samples from Degussa and Altair (\(D = 21\) and 30 – 50 nm respectively).\(^2\,^3\) Error bars for each estimated grain size were determined by collecting three XRD spectra per sample, each for a different area of the sample surface, and then calculating the standard deviation of the grain sizes estimated from those three spectra.

Brunauer-Emmett-Teller (BET) surface areas were determined from \(\text{N}_2\) adsorption onto the titania powders using a Micromeritics ASAP 2010 apparatus. Samples were degassed for several hours at 150 °C (except the samples synthesized at 140 °C, which were degassed at room temperature) prior to the \(\text{N}_2\) adsorption analysis, which was carried out at liquid nitrogen temperature (-196 °C).
Transmission electron micrographs (TEM) were taken on a JEOL 2010 microscope. Each TEM sample was prepared by evaporating 1-5 drops of a sonicated ethanol suspension of titania onto a 300-mesh copper / carbon grid (Ted Pella, Inc.).

Raman spectra were taken on a Renishaw Ramascope apparatus using a He-Ne laser with an excitation wavelength of 633 nm. Collection times ranged from 10 to 60 seconds per spectrum.

Differential thermal analysis (DTA) was performed in air on a Thermal Advantage SDT 2960 apparatus using a temperature range of 25-600 °C and a heating rate of 20 °C min⁻¹.

3.3. Results and discussion

The hydrothermal synthesis reported in this work yielded phase-pure anatase nanocrystals, the physical properties of which were tunable through variations in the reaction conditions. The reaction temperature, precursor concentration, and hydrolysis ratio were all found to have an effect on the primary particle size and, thus, the specific surface area of the product. In particular, very fine (< 10 nm) grain sizes and correspondingly large (up to 250 m² g⁻¹) surface areas were observed at low temperatures, low precursor concentrations, and intermediate hydrolysis ratios.

In addition to its influence on particle size, the reaction temperature determined the morphology of the nanocrystals; lower temperatures yielded almost exclusively
Figure 3.1. X-ray diffraction spectra of hydrothermal anatase produced at (A) 140 °C, (B) 150 °C, (C) 220 °C, and (D) 300 °C. In all cases, the samples’ XRD peaks indicate the exclusive formation of anatase-phase titania. The gradual narrowing of anatase linewidths with increasing temperature reflects an increase in average crystallite size.

spherical particles, while at higher temperatures a mixture of small spherical and large cubic particles was observed. The bimodal distribution of sizes and morphologies present in the latter case suggested that grain growth takes place via Ostwald ripening at high temperatures.

Finally, a combination of Raman spectroscopy and differential thermal analysis revealed that the thermal stability of hydrothermal titania depends critically on the reaction temperature. Samples prepared at 150 °C and above were thermally stable up to 600 °C, whereas samples prepared below 140 °C had poor thermal stability due to their low crystallinity.
3.3.1. Size, Shape, and Surface Area

Figure 3.1 shows the X-ray diffraction patterns of hydrothermal titania prepared at temperatures between 140 and 300 °C. In all reactions for which \( T \geq 140 \) °C the products were found to consist of phase-pure anatase, which is consistent with previous findings that anatase formation is favored at or near neutral pH under higher-temperature hydrothermal conditions.\(^4-7\) It is interesting that even at temperatures as low as 140 °C, it is possible to obtain a crystalline product; the ability to process nanocrystalline anatase at such a low temperature is advantageous both because it requires less energy for manufacturing and because lower temperatures tend to result in the formation of finer crystallites with larger specific surface areas.\(^7-9\)

The gradual narrowing of the XRD lines with increasing temperature reflects a corresponding increase in the average grain size (\( D \propto \beta^{-1} \)), a trend that is quantitatively illustrated for two different hydrolysis ratios (\( r = 5 \) and \( r = 20 \)) in Figure 3.2. There appears to be very little difference between the size versus temperature plots for these two hydrolysis ratios; however, as will be discussed in the following section, it is possible that at intermediate hydrolysis ratios one could obtain even finer anatase crystallites than for reactions run with an excess of either water or alkoxide precursor.

A series of samples prepared with \( r = 20 \) and \([\text{Ti(OEt)}_4] = 0.02\) mol L\(^{-1}\) at various temperatures was characterized by BET surface area measurements, the results of which were then compared to "expected" surface areas calculated from the XRD-derived grain sizes. Such an analysis can reveal whether particles contain defects and/or aggregates, both of which can result in lower BET surface areas than expected from the crystallite
Figure 3.2. Effect of reaction temperature on average grain size of hydrothermally prepared anatase for hydrolysis ratios of $r = 20$ (●) and $r = 5$ (○). Samples were prepared using a Ti(OEt)$_4$ concentration of 0.02 mol L$^{-1}$ and a total reaction time of 2 h. At both $r$-values the crystallite size increases with the reaction temperature. Hydrolysis ratios of 5 and 20 appear to yield similar grain sizes for a given set of hydrothermal conditions.

The expected surface area of a sample was computed assuming perfectly spherical, unaggregated crystallites with a grain size determined by the XRD analysis and a mass density equal to that of bulk anatase, i.e., $\rho = 3.84$ g cm$^{-3}$. Table 3.1 shows the grain sizes (D), experimental surface areas ($S_{\text{BET}}$), and expected surface areas ($S_{\text{Expected}}$) for the ($r = 20$, [Ti(OEt)$_4$] = 0.02 mol L$^{-1}$) samples prepared in this work as well as for two commercial nano-TiO$_2$ samples obtained from Degussa (P25) and Altair (TiNano).

Three features of these data are particularly noteworthy. First, by using a very low hydrothermal reaction temperature ($T = 140 \, ^{\circ}\text{C}$), it is possible to prepare nanocrystalline
Table 3.1. Grain sizes and specific surface areas for hydrothermal titania prepared with [Ti(OEt)$_4$]=0.02 mol L$^{-1}$ and r=20. The results indicate that hydrothermal synthesis in ethanol produces ultrafine anatase with a specific surface area up to 5 times that of commercial nano-titania. Experimental surface areas are consistently 63-86% of their expected values, indicating that some of the anatase particles form hard aggregates while other particles are either unaggregated or loosely aggregated.

<table>
<thead>
<tr>
<th>T (°C) or company</th>
<th>d (nm)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{Expected}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{BET}$:$S_{Expected}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>5.35</td>
<td>250.6 ± 3.4</td>
<td>292.1</td>
<td>0.858</td>
</tr>
<tr>
<td>150</td>
<td>6.69</td>
<td>160.7 ± 0.7</td>
<td>233.6</td>
<td>0.688</td>
</tr>
<tr>
<td>200</td>
<td>7.72</td>
<td>---</td>
<td>202.4</td>
<td>---</td>
</tr>
<tr>
<td>220</td>
<td>8.85</td>
<td>127.7 ± 0.7</td>
<td>176.6</td>
<td>0.723</td>
</tr>
<tr>
<td>250</td>
<td>8.81</td>
<td>123.1 ± 0.9</td>
<td>177.4</td>
<td>0.694</td>
</tr>
<tr>
<td>275</td>
<td>16.70</td>
<td>---</td>
<td>93.6</td>
<td>---</td>
</tr>
<tr>
<td>300</td>
<td>16.17</td>
<td>60.8 ± 1.5</td>
<td>96.6</td>
<td>0.629</td>
</tr>
<tr>
<td>335</td>
<td>19.97</td>
<td>55.0 ± 0.9</td>
<td>78.2</td>
<td>0.703</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>~ 21</td>
<td>50 ± 15</td>
<td>74.4</td>
<td>0.672</td>
</tr>
<tr>
<td>Altair TiNano</td>
<td>30-50</td>
<td>50 ± 10</td>
<td>31.3-52.1</td>
<td>0.960-1.597</td>
</tr>
</tbody>
</table>

anatase with a surface area of up to 250 m$^2$ g$^{-1}$. Secondly, all of the samples prepared in this work possess larger surface areas than those reported for commercial titania samples; this is most likely due to the strategy of using a mild hydrothermal treatment optimized to produce fine grains (and consequently larger surface areas). The aerosol methods by which Degussa and Altair manufacture their products cannot be easily controlled to provide grain sizes below 20 nm, and as a consequence their specific surface areas tend to be low (~ 50 m$^2$ g$^{-1}$).$^{2,3}$ Finally, comparison of the experimental and expected surface areas for the hydrothermally prepared powders indicates that our synthesis consistently yields a product with 63-86% of its ideal surface area, i.e., the surface area one would expect for a sample consisting of completely deaggregated crystallites.
The significance of this last observation is that due to the absence of a surface stabilizing (peptizing) agent in the reaction medium, some of the primary particles in the product either contain defects that reduce their surface area or else form hard aggregates whose surfaces are unavailable for sorption. Because ultrafine (< 10 nm) crystals tend to have a very low number of defects, it is likely that the presence of hard aggregates in the product is responsible for the difference between the experimental and expected values for the specific surface areas of the hydrothermal samples. Even so, a sufficient fraction of primary particles remain either unaggregated or loosely aggregated so that reasonably high surface areas are observed.

Figure 3.3 shows transmission electron micrographs that corroborate both the temperature dependence of grain size and the interpretation of the BET data; in addition to the obvious increase in average crystallite size from the 150 °C (Figure 3.3a) sample to the 300 °C sample (Figure 3.3b), it is clear from these images that in both samples some individual crystallites form hard aggregates in which only a fraction of each primary particle’s surface area is available for sorption, while other crystallites form relatively loose aggregates in which the total available surface area is higher.

The most striking revelation in the TEM images, however, is that temperature has a pronounced effect on particle morphology and distribution. Specifically, the particle sizes and shapes appear to shift from a unimodal distribution of roughly spherical crystals at 150 °C to a bimodal distribution, consisting mostly of 10 – 15 nm spheres with a smaller number of ~40 nm cubes, at 300 °C. The appearance of larger particles with new morphology at the latter temperature suggests that higher reaction temperatures are conducive to grain growth via a dissolution-reprecipitation mechanism (i.e., Ostwald
Figure 3.3. TEM images of hydrothermal anatase prepared at (a) 150 °C and (b) 300 °C. Lower reaction temperatures produce predominantly small (< 10 nm), spherical primary particles, while higher reaction temperatures result in a bimodal distribution of small spherical and larger cubic nanocrystals.

ripening) in which larger particles grow at the expense of smaller ones. The relatively small fraction of large cubes present in the 300 °C product is most likely due to the hydrothermal reaction time (2 h), which is considerably shorter than the treatment times (1 or more days) used in other studies (e.g., Wang et al). An increase in aging time would presumably result in more extensive Ostwald ripening and consequently a greater number of large cubic nanocrystals.
Figure 3.4 shows the effect of initial Ti(OEt)$_4$ concentration on anatase grain size for a series of samples prepared with a hydrolysis ratio of $r = 20$ at 220 °C. Clearly an increase in the precursor concentration results in the formation of larger crystallites, which is to be expected since more material is available for growth onto each crystal after nucleation. However, the grain sizes start to increase more slowly once [Ti(OEt)$_4$] exceeds 0.04 – 0.05 mol L$^{-1}$, which suggests that at higher supersaturations the process of nucleation competes with grain growth to a greater extent than at low supersaturations.

**Figure 3.4.** Effect of precursor concentration on average grain size of hydrothermally prepared anatase. Samples were prepared at 220 °C using a hydrolysis ratio of $r = 20$ and a total reaction time of 2 h. Higher initial Ti(OEt)$_4$ concentrations tend to produce coarser nanocrystals.
The effect of the hydrolysis ratio on grain size was studied for a group of reactions conducted at 220 °C using \([\text{Ti(OEt)}_4] = 0.02 \text{ mol L}^{-1}\) and a total reaction time of 2 h. Figure 3.5 shows the results of varying the hydrolysis ratio between \(r = 1\) and \(r = 100\) under these conditions. The plot of crystallite size as a function of hydrolysis ratio exhibits a minimum between \(r\)-values of 5 and 15. At low \(r\) values, i.e., \(1 \leq r \leq 10\), the results of the present work are in qualitative agreement with previous reports that an increase in the hydrolysis ratio favors the formation of finer crystallites.\(^4\)\(^10\) However, above a hydrolysis ratio of \(r \simeq 15\), the grain size data obtained here begin to follow an upward trend as \(r\) further increases.

**Figure 3.5.** Effect of hydrolysis ratio on average grain size of hydrothermally prepared anatase. Samples were prepared at 220 °C using a Ti(OEt)\(_4\) concentration of 0.02 mol L\(^{-1}\) and a total reaction time of 2 h. The occurrence of a minimum grain size in the range \(r = 5 - 15\) suggests competition between accelerated nucleation and hydrogen bond-facilitated agglomeration upon an increase in the hydrolysis ratio.
It is likely that the data shown in Figure 3.5 reflect a competition between two or more factors. One possible explanation for the observation of minimal sizes at intermediate $r$ values is that an increase in $r$ results in both (a) an increase in the anatase nucleation rate, which favors finer crystallites, and (b) enhanced hydrogen bonding among the nuclei once they form, a process that favors grain growth. The former effect could arise from a faster, more complete hydrolysis of the precursor, which would encourage the formation of a large number of anatase nuclei in a short amount of time.\textsuperscript{5} On the other hand, one can also expect more extensive hydrogen bonding among anatase nuclei at high $r$ values than at low $r$ values, which would tend to promote the agglomeration of those nuclei to eventually form coarser primary particles.\textsuperscript{11} If anatase nucleation and hydrogen bonding are indeed competitive processes in the present hydrothermal synthesis, it follows that the smallest crystallites would be obtained at $r$-values for which accelerated nucleation is the dominant effect. Based on the results in Figure 3.5, the enhanced nucleation rate appears to dominate over hydrogen bond-facilitated growth at intermediate $r$-values ($5 \leq r \leq 15$), whereas the reverse is true at very low ($r < 5$) or very high ($r > 15$) hydrolysis ratios.

3.3.2. Amorphous Content and Thermal Stability

Both Raman spectroscopy and differential thermal analysis (DTA) were used to assess the amorphous content of hydrothermal titania samples prepared at different temperatures. For these analyses, a control sample consisting entirely of amorphous TiO$_2$ was prepared by hydrolyzing Ti(OEt)$_4$ in dry ethanol solvent inside the bomb at 25 °C. Figure 3.6 shows the evolution of the samples’ Raman spectra with an increase in
**Figure 3.6.** Evolution of TiO$_2$ Raman spectra with reaction temperature. Samples were prepared at (A) 25 °C, (B) 140 °C, (C) 150 °C, and (D) 220 °C using a hydrolysis ratio of $r = 20$, a Ti(OEt)$_4$ concentration of 0.02 mol L$^{-1}$, and a total reaction time of 2 h. The spectra indicate an increase in crystallinity with increasing reaction temperature; complete crystallinity is achieved at temperatures as low as 150 °C.

![Raman spectra](image)

reaction temperature. The results indicate that even at temperatures as low as 150 °C, a completely crystalline product is obtained; however, for temperatures below 150 °C there is an increasing amount of amorphous material as the temperature is lowered further, until a completely amorphous solid is observed for a room-temperature reaction.

Differential thermal analysis (DTA) of the hydrothermal samples corroborates the Raman spectroscopic evidence of increased crystallinity at higher reaction temperatures. Figure 3.7a, which shows the DTA profiles of samples prepared at or below 220 °C, illustrates the gradual disappearance of amorphous material as the reaction temperature is increased. Samples containing amorphous titania typically exhibit an exothermic DTA...
peak between 350 and 450 °C, indicating crystallization of amorphous material to the anatase phase.\textsuperscript{12,13} In the control sample prepared at 25 °C (curve A), crystallization is observed at approximately 425 °C, while the samples prepared at 100 and 140 °C (curves B and C) exhibit crystallization peaks at 350 and 375 °C respectively. Once the reaction temperature is raised to 150 °C (curve D), the product is 100 % crystalline, as evidenced by the complete disappearance of the exothermic amorphous $\rightarrow$ anatase transition peak.

The decrease in crystallization temperature from the 25 °C control sample to the 100 °C sample indicates that some crystalline material is forming even at 100 °C; as has been reported by several authors, the presence of a small amount of crystalline material in an otherwise amorphous sample reduces the temperature at which the amorphous material crystallizes.\textsuperscript{12, 14-16} On the other hand, increasing the hydrothermal reaction temperature from 100 to 140 °C causes a slight increase in crystallization temperature (from 350 to 375 °C). It may be that in samples processed at higher temperatures, the amorphous materials are denser than those prepared at lower temperatures and therefore require greater thermal energy to dissolve and subsequently crystallize.

Also of interest are the changes observed in the anatase $\rightarrow$ rutile phase transformation temperature as a function of reaction temperature. Like the crystallization of amorphous titania to anatase, the anatase $\rightarrow$ rutile transition manifests itself as an exothermic peak in a sample’s DTA profile. The exact temperature at which the anatase $\rightarrow$ rutile transformation occurs can vary greatly depending on a number of factors, including crystallinity, phase purity, grain size, and preparation method.\textsuperscript{5, 10, 17} In the present work, the conversion of anatase to rutile is observed within the temperature range studied (i.e., below 600 °C) only for those titania samples prepared below 140 °C, while
Figure 3.7. (a) Evolution of differential thermal analysis (DTA) spectra with reaction temperature. Samples were prepared at (A) 25 °C, (B) 100 °C, (C) 140 °C, (D) 150 °C, and (E) 220 °C. Samples prepared below 140 °C exhibit the amorphous $\rightarrow$ anatase and anatase $\rightarrow$ rutile transitions at low temperature and in rapid succession, indicating poor crystallinity in these samples. The absence of exothermic peaks in the DTA profile for samples prepared above 140 °C suggests good thermal stability. (b) Influence of reaction temperature on DTA crystallization temperatures. The decrease in crystallization temperature from the 25 °C sample (curve A) to the 100 °C sample (curve B) is attributable to the presence of anatase nuclei ("seeds") in the latter sample. The subsequent increase in crystallization temperature from the 100 °C sample (curve B) to the 140 °C sample (curve C) possibly results from an increase in sample density.
no phase change appears to take place for samples synthesized at 150 °C or higher. The 25 °C control sample exhibits the anatase → rutile peak at roughly 475 °C, whereas the 100 °C sample undergoes the phase transformation at a considerably lower temperature of 390 °C. In both these cases, the conversion to rutile either overlaps with or occurs immediately after the crystallization of amorphous material to anatase (Figures 3.7a and 3.7b), indicating that the samples have very low thermal stability. This result can most likely be attributed to the very large fraction of amorphous material present in these samples. By contrast, the anatase in the samples prepared at 140 °C and above is thermally stable at least up to 600 °C, as evidenced by the absence of an anatase → rutile peak in their DTA profiles; this result is more consistent with the existing literature, in which investigators typically report thermal stability up to 650-1000 °C, having started with samples that are already highly crystalline before heat treatment.5,9,18

Figure 3.8 shows XRD spectra for the heat-treated samples in the present work; these spectra confirm that the low-crystallinity titania samples prepared below 140 °C contain both anatase and rutile after heat treatment, while the high-crystallinity samples prepared at or above 140 °C consist entirely of anatase even after heating to 600 °C and are therefore thermally resistant to conversion to rutile. Additionally, the heat-treated 100 °C sample contains a smaller fraction of rutile than the heat-treated 25 °C control sample, suggesting that the slightly higher crystallinity of the as-prepared 100 °C sample renders it more thermally stable against the anatase → rutile transformation. In this case, then, a higher degree of crystallinity correlates with increased thermal stability. Because no grain size data are available for the samples prepared at 25 and 100 °C, no correlation can be made at this time between thermal stability and grain size.
Figure 3.8. XRD spectra of hydrothermal TiO$_2$ samples after heating to 600 °C in a differential thermal analyzer. Original preparation temperatures were (A) 25 °C, (B) 100 °C, (C) 140 °C, and (D) 150 °C. Thermal treatment results in the formation of rutile only in the samples prepared at lower temperatures (curves A and B), which confirms the higher thermal stability of the samples prepared above 140 °C (curves C and D). The decrease in rutile content from the treated 25 °C sample (curve A) to the treated 100 °C sample (curve B) indicates that the latter is more thermally stable, most likely due to the presence of small amounts of crystalline material in the 100 °C sample prior to DTA.

3.4. Summary and future work

A mild hydrothermal synthesis (< 200 °C, 2 h) has been used to prepare ultrafine, phase-pure nanocrystalline anatase with specific surface area up to 5 times that of commercially available nano-titania. The physical properties of the hydrothermal product can be fine-tuned by adjusting the temperature, precursor concentration, and hydrolysis ratio of the reaction. It is possible to obtain a very fine-grained crystalline product with high thermal stability and ultra-high surface area using reaction temperatures as low as
140 – 150 °C. The results of this work suggest that the grain size might be reduced even further by optimizing the concentration of alkoxide precursor and the water:alkoxide ratio. Possible future studies include testing very high initial alkoxide concentrations to determine whether a maximum grain size exists, monitoring grain growth by TEM in order to better understand the temperature dependence of Ostwald ripening, and investigating the factors that determine the crystallization temperature in samples prepared below 140 °C.

References


Chapter 4

Growth modeling of monodisperse TiO$_2$ nanoparticles in solution

4.1. Introduction

In Chapter 3 it was shown that reasonably monodisperse anatase-phase TiO$_2$ nanoparticles could be produced using a simple hydrothermal synthesis that afforded good control over various physical properties, especially particle size. For such a synthesis to be viable on a large scale, however, it is necessary that one be able to quantitatively predict nanoparticle sizes and growth rates given a specific set of reaction conditions. This in turn requires the ability to calculate values for kinetic and thermodynamic constants, such as the surface tension and the surface reaction activation energy, that govern the growth of nanocrystals. Considerable work has been done to develop and apply particle growth models to both isotropic and anisotropic crystals in the past,$^{1-23}$ but to the author's knowledge only two studies specific to the nanometer scale have been published, neither of which has yet been applied to nanocrystalline TiO$_2$.\textsuperscript{18,22} As part of the present work, therefore, a simple growth model was used to extract various kinetic and thermodynamic growth parameters for hydrothermal anatase synthesis.

This chapter describes the basic principles and derivation of the model, a comparison of the model with experimental growth data, and a suggested scheme for calculating values of parameters related to the interfacial reactions involved in particle growth. At the end of the chapter, the advantages and limitations of the model will be briefly summarized, along with suggestions for future growth modeling studies with nanoparticle systems.
4.2. The single-particle growth model\textsuperscript{24}

The first step in deriving any particle growth model is to consider the simplest case of a single, isolated nanoparticle growing in a solution of homogeneously dispersed monomer at a constant temperature T. The particle surface is separated from the bulk monomer solution by a region called the diffusion layer, in which a monomer concentration gradient drives the migration of monomer from the solution to the surface until the particle has grown via monomer addition to its equilibrium size (i.e., until the concentration gradient is reduced to zero). For simplicity the following five assumptions are made: (1) there is only one kind of monomer present in the solution; (2) the particle is spherical and grows at an equal rate in all directions; (3) the pseudo-steady state approximation holds, that is, the concentration gradients in the particle’s diffusion layer are established much faster than the particle surface moves; (4) the forward and reverse surface reactions (i.e., monomer addition and monomer removal from the particle, respectively) follow linear kinetics; and (5) the transport of monomer across the diffusion layer is governed by Brownian motion. The mathematical consequences of each assumption will be identified at appropriate points in the development of the single-particle growth model laid out below.

4.2.1. Computing the monomer concentration at the solid-solution interface

Figure 4.1 shows a spherical particle of radius r surrounded by a diffusion layer of thickness \( \delta \). The variables \( c_b \), \( c_e \), and \( c_i \) denote the bulk monomer concentration, the equilibrium solubility of the particle, and the monomer concentration at the particle-
solution interface, respectively. It is this last quantity, $c_i$, that must be computed in order to determine the growth rate for the particle.

Before deriving an expression for $c_i$, it is useful to make two qualitative observations about the quantity’s physical significance. First, the relationship between $c_i$ and the equilibrium solubility $c_e$ determines whether the particle grows, dissolves, or remains the same size. If $c_i > c_e$, as shown in the figure, then the particle will grow; if $c_i < c_e$, dissolution will occur. When the two concentrations are equal, i.e., when the interfacial concentration has reached its equilibrium value, then there is no driving force for either growth or dissolution and the particle size remains constant.

Secondly, the difference between $c_i$ and the bulk concentration $c_b$ governs the rate at which monomer is transported across the diffusion layer to the particle surface. Note, however, that this diffusion rate does not necessarily determine the rate of particle growth. Specifically, if the rate of monomer reaction at the surface to form new bonds is much slower than monomer diffusion, then the surface reaction rate is what ultimately determines the growth rate ("reaction-controlled" growth). If, on the other hand, monomer diffusion is much slower than the surface reaction, then diffusion is the rate-determining process ("diffusion-controlled" growth).

Now that the physical importance of $c_i$ has been established, the remainder of this section will be devoted to the mathematical analysis of the concentration profile of the diffusion layer. The assumption of a spherical particle allows one to treat the simplest possible case of the three-dimensional diffusion problem. The general three-dimensional diffusion equation for the spherical geometry shown in Figure 4.1 is:
Figure 4.1. Schematic illustration of a growing nanoparticle (NP) with radius r and diffusion layer thickness δ. The variables $c_b$, $c_i$, and $c_e$ represent the bulk monomer concentration, the concentration at the liquid-solid interface, and the equilibrium solubility of the solid respectively.
\[ \frac{\partial c(x, t)}{\partial t} = \frac{1}{x^2} \frac{d}{dx} \left( x^2 D \frac{\partial c(x, t)}{\partial x} \right) \]  \hfill (4.1)

where \( c(x,t) \) is the monomer concentration, \( D \) is the diffusion coefficient, \( t \) is the time, and \( x \) is the distance from the center of the growing nanoparticle. The boundary conditions for this problem are:

\[ c|_{x=r+\delta} = c_b \]  \hfill (4.2a)

and

\[ D \frac{\partial c}{\partial x}|_{x=r} = k_s (c_i - c_e) \]  \hfill (4.2b)

while the initial condition is:

\[ c(r, 0) = c_0(r) \]  \hfill (4.3)

Boundary condition (4.2a) arises because the monomer concentration at the outer surface of the diffusion layer is necessarily equal to the monomer concentration of the adjacent bulk solution. Boundary condition (4.2b) describes the relationship between the rate of monomer diffusion at the particle surface and the rate of surface reaction; recall that the latter process has been assumed to follow linear kinetics, i.e., that for a given temperature the reaction rate is related by a proportionality “constant” \( k_s \) to the amount of monomer
present in excess of the particle’s equilibrium solubility. It should be noted that $k_s$ is not a true constant because of its Arrhenius-type dependence on temperature:

$$k_s = k_0 \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (4.4)

where $E_a$ is the activation energy for the surface reaction, $R$ is the gas constant, $T$ is the temperature, and $k_0$ is a system-dependent preexponential constant. Recent nanoparticle growth models have tended to neglect this temperature dependence of $k_s$,\textsuperscript{18,22} but as will be seen shortly, even a temperature change of 10 K (or 10 °C) can change the value of $k_s$ by nearly a factor of 2.

The general spherical diffusion problem is further simplified when validity of the pseudo-steady state approximation is assumed. If concentration gradients are established much faster than the particle surface moves, it is possible to treat the surface monomer concentration as essentially constant in time, so that one can set the left-hand side of Equation (4.1) equal to zero. Then the diffusion equation becomes:

$$0 = \frac{1}{x^2} \frac{d}{dx} \left( x^2 D \frac{\partial c(x, t)}{\partial x} \right), \hspace{1cm} r < x < r + \delta$$  \hspace{1cm} (4.5)

with the same boundary and initial conditions as before.

The analytical solution of Equation (4.5) is:
\[ c_b - c(x) = \frac{k_x r}{D}(c_i - c_e) \left( \frac{1}{x} - \frac{1}{r + \delta} \right) \]  \hspace{1cm} (4.6)

Because it has been assumed that monomer diffusion is controlled by Brownian motion, the diffusion layer thickness \( \delta \) may be computed as:

\[ \delta = \sqrt[4]{\frac{3T}{2}} \left( \frac{D^2 \mu}{\rho_f} \right)^{1/6} \left( \frac{\pi \rho_x}{k_B T} \right)^{1/4} r^{3/4} \]  \hspace{1cm} (4.7)

At the particle surface, i.e., at \( x = r \), Equation (4.6) becomes:

\[ c_b - c_i = Da \left( c_i - c_e \right) \left( \frac{\delta}{r + \delta} \right) \]  \hspace{1cm} (4.8)

where \( Da \) is the “Damköhler number” defined as:

\[ Da \equiv \frac{k_x r}{D} \]  \hspace{1cm} (4.9)

Rearrangement of Equation (4.8) gives an expression for the monomer concentration at the particle-solution interface:
\[ c_i = \frac{c_b + c_e Da \left( \frac{\delta}{r + \delta} \right)}{1 + Da \left( \frac{\delta}{r + \delta} \right)} \]  \tag{4.10}

Finally, since the size-dependent equilibrium solubility \( c_e \) is given by the Gibbs-Thomson equation as

\[ c_e = c_\infty \exp \left( \frac{2\gamma V_m}{rRT} \right) \]  \tag{4.11}

one may write

\[ c_i = c_b + c_\infty \exp \left( \frac{2\gamma V_m}{rRT} \right) Da \left( \frac{\delta}{r + \delta} \right) \]  \tag{4.12}

where \( \gamma \) is the surface tension, \( V_m \) is the molar volume of the solid material, and \( c_\infty \) is the equilibrium solubility for an infinite flat surface.

**4.2.2. Computing the growth rate**

Having obtained an expression for \( c_i \), one can now readily compute the single-particle growth rate. The rate of change of the particle volume \( v \) is:
\[
\frac{dv}{dt} = \frac{d}{dt}\left(\frac{1}{V_m} \frac{4}{3} \pi r^3 \right) = \frac{4\pi}{V_m} r^2 \frac{dr}{dt}
\]  
(4.13)

On the other hand, \(dv/dt\) can also be considered as the product of the surface reaction rate multiplied by the total surface area of the particle, i.e.,

\[
\frac{dv}{dt} = \left[k_s (c_i - c_e)\right] \times 4\pi r^2
\]  
(4.14)

Setting the right-hand sides of Equations (4.13) and (4.14) equal to each other, and substituting (4.11) and (4.12) for \(c_e\) and \(c_i\) respectively, one obtains the following expression for the single-particle growth rate:

\[
\frac{dr}{dt} = \frac{k_s V_m \left[ c_b - c_\infty \exp\left(\frac{2\gamma V_m}{rRT}\right)\right]}{1 + Da \left(\frac{\delta}{r + \delta}\right)}
\]  
(4.15)

Physically, this equation can be interpreted as follows: \(k_s V_m\) represents the surface reaction rate; \([c_b - c_\infty \exp (2\gamma V_m/rRT)]\) is the excess monomer concentration; and the denominator \(\{1 + Da[\delta/(r+\delta)]\}\), which contains the Damköhler number (\(Da = k_s r/D\)), determines whether the particle growth is diffusion- or reaction-controlled.

4.2.3. Monomer mass balance
Because nanoparticle growth is accompanied by the depletion of monomer from the bulk solution, it is necessary to couple the growth rate Equation (4.15) with a monomer mass balance equation, i.e., an equation for $\frac{dc_b}{dt}$. The bulk monomer concentration $c_b$ is equal to the total number of moles of bulk monomer divided by the total solution volume:

$$c_b = \frac{n}{V_{sln}} \quad \text{(4.16)}$$

Taking the derivative with respect to time, and assuming that the solution volume does not change, one obtains

$$\frac{dc_b}{dt} = \frac{1}{V_{sln}} \frac{dn}{dt} \quad \text{(4.17)}$$

Now, in the interval $dt$, the particle volume increases by an amount $dv = 4\pi r^2 \, dr$, consuming $dn$ moles in the process. The number of moles contained in the volume $dv$ is just $dv/V_m$, and so one may write:

$$\frac{dn}{dt} = \frac{1}{V_m} \frac{dv}{dt} = \frac{4\pi r^2}{V_m} \, dr \quad \text{(4.18)}$$

Substitution of (4.18) into (4.17) yields an equation for the monomer depletion rate as a function of the nanoparticle radius:
\[ \frac{dc_b}{dt} = \frac{4\pi r^2}{V_m V_{sm}} \frac{dr}{dt} \quad (4.19) \]

It is also possible to treat a fixed number \( N \) of identical particles, i.e., a perfectly monodisperse sample, simply by multiplying the right side of Equation (4.19) by \( N \):

\[ \frac{dc_b}{dt} = \frac{4N\pi r^2}{V_m V_{sm}} \frac{dr}{dt} \quad (4.20) \]

Simultaneous solution of the differential equations (4.15) and (4.20) allows one to compute the growth curve for a constant number \( N \) of isolated spherical particles of any material, given an initial bulk monomer concentration \( c_0 \) and an initial particle radius \( r_0 \). Since \( N \) is kept constant, this problem only applies in cases where nucleation and growth do not overlap.

4.3. Application of the single-particle growth model to hydrothermally derived anatase nanocrystals

4.3.1. Computer code and parameter assignment

Using the model developed above, a MATLAB code was written to treat \( N \) identically sized, spherical, anatase-phase TiO\(_2\) nanoparticles (molar volume = \( V_m = 2.08 \times 10^{-5} \) m\(^3\) mol\(^{-1}\), density = \( \rho_s = 3.84 \times 10^6 \) g m\(^{-3}\)) prepared in ethanol (density = \( \rho_r = 8.0 \times 10^{-5} \) g m\(^{-3}\), viscosity = \( \mu = 1.08 \) g m\(^{-1}\) s\(^{-1}\)) under hydrothermal conditions as described in
Chapter 3; the text of this program is included in the Appendix. By fitting experimental anatase growth data with curves generated by this code, it was possible to determine an approximate value for the surface reaction rate parameter \( k_s = k_0 \exp(-E_a/RT) \) which, upon comparison with typical diffusivity values (\( D \sim 10^{-10} \text{ m}^2 \text{ s}^{-1} \)), qualitatively established whether the hydrothermal growth of anatase nanoparticles was diffusion- or reaction-controlled.

The MATLAB code accepted globally defined input values for \( \gamma, N, D, T, k_0, \) and \( E_a, \) and then used those values to calculate the growth profile for any initial monomer concentration \( c_0 \) and any initial particle radius \( r_0 \). The program simulated a reaction volume of \( V_{\text{sln}} = 1.0 \times 10^{-9} \text{ m}^3 \), and the value of \( c_\infty \) for anatase was assumed to be on the order of \( 10^{-2} \text{ mol m}^{-3} \) (the magnitude of this latter parameter is in fact unknown but is probably comparable to that used in other semiconductor nanoparticle growth simulations).\(^{22}\)

The values of \( c_0, \rho_s, \rho_t, \mu, \) and \( T \) were assigned according to the experimental conditions that were to be used in actual hydrothermal anatase syntheses to test the model (see also Section 4.3.2). The initial concentration \( c_0 \) of monomer (titanium (IV) ethoxide in this case) was set to 320 \( \text{ mol m}^{-3} \) and \( T \) was set to 423 or 433 K (150 or 160 °C respectively). The parameters \( \gamma \) and \( D \) were assigned typical values used in other theoretical particle growth studies (\( \gamma = 0.1 \text{ J m}^{-2}, D = 10^{-10} \text{ m}^2 \text{ s}^{-1} \)).\(^{22}\) An initial particle radius of \( r_0 = 5 \times 10^{-10} \text{ m} \) was assumed, and the values of \( k_0 \) and \( E_a \) were allowed to vary in order to fit code-generated curves to experimental data.
4.3.2. Fitting growth curves to experimental grain size data: estimation of $k_s$ and determination of rate-controlling process in particle growth

Two anatase nanocrystal growth experiments were run using the same general experimental setup and procedure detailed in Chapter 3; the reaction temperatures tested were 423 and 433 K. In both cases, the initial concentration was 320 mol m$^{-3}$ (0.32 mol L$^{-1}$), the hydrolysis ratio ([H$_2$O]/[Ti(OEt$_4$)]) was 20, and the total reaction time was 7200 s (2 h). Aliquots were withdrawn at predetermined intervals, evaporated, dried, mixed with silicon powder, and characterized by X-ray diffraction (XRD) as described in Chapter 3. Grain sizes were estimated using the Debye-Scherrer formula with Warren’s correction for instrumental broadening. The final grain size in each experiment was used to calculate the total number $N$ of anatase nanoparticles as follows: first, under the assumption that the anatase particles were unaggregated spheres, each with radius $r = 0.5 \times \text{(final grain size)}$, the volume of a single nanoparticle was computed as:

$$v_{NP} = \frac{4\pi r^3}{3} \quad (4.21)$$

Then, using the density of anatase ($\rho_s = 3.84 \times 10^6$ g m$^{-3}$), the mass of each particle was calculated according to:

$$m_{NP} = v_{NP} \times \rho_s \quad (4.22)$$
Finally, the total number of particles was determined by dividing the theoretical total mass of product in the simulated volume \((m_{\text{tot}} = c_0 V_{\text{sh}} \times \text{(molar mass of anatase)} = 2.56 \times 10^{-5} \text{ g})\) by the mass of one nanoparticle:

\[
N = \frac{m_{\text{tot}}}{m_{\text{NP}}} = \frac{2.56 \times 10^{-5} \text{ g}}{m_{\text{NP}}} \tag{4.23}
\]

Grain sizes estimated from XRD linewidths were plotted as a function of time, and the resulting graph was fitted with N-particle growth curves generated by MATLAB for different combinations of \(k_0\) and \(E_a\), using the value of \(N\) calculated from Equation (4.23). The experimental data sets and their various fits are shown in Figure 4.2; the \(k_s\) values obtained from each reasonably good fit (i.e., from each curve generated using a different \((k_0, E_a)\) combination), along with the calculated values of \(N\), are listed for the two temperatures in Table 4.1. As yet no quantitative evaluation has been done with respect to the “goodness” of each fit; thus the results shown in Figure 4.2 and Table 4.1 should only be regarded as preliminary and semiquantitative.

Three general results are worth noting: first, at a given temperature, each fitted curve corresponded to a combination of \(k_0\) and \(E_a\) that yielded roughly the same \(k_s\) value. At 423 K (150 °C), for example, each \((k_0, E_a)\) pair that yielded a qualitatively good fit gave a \(k_s\) value of \(3.1 - 3.4 \times 10^{-10} \text{ s}^{-1}\). Interestingly, this consistency in \(k_s\) values was observed despite the widely varying values of \(k_0\) and \(E_a\) that generated good fits to the experimental data.
Figure 4.2. Experimental nano-anatase growth data (o) fitted with the single-particle growth model as applied to N identical dots growing at (a) 423 K (150 °C) and (b) 433 K (160 °C). The calculated values of N were $2.00 \times 10^{13}$ and $1.88 \times 10^{13}$ for 423 K and 433 K respectively. Each colored line represents a fit obtained using a different combination of the preexponential constant $k_0$ and activation energy $E_a$; these values are identified with the corresponding curves on each graph.
Table 4.1. Single particle growth model parameters calculated from experimental growth data for anatase nanoparticles.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Final grain size (nm), experimental</th>
<th>Calculated N</th>
<th>$k_0$ (s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Calculated $k_s$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>8.56</td>
<td>$2.00 \times 10^{13}$</td>
<td>$5.00 \times 10^{-4}$</td>
<td>50</td>
<td>$3.35 \times 10^{-10}$</td>
</tr>
<tr>
<td>423</td>
<td>8.56</td>
<td>$2.00 \times 10^{13}$</td>
<td>700</td>
<td>100</td>
<td>$3.13 \times 10^{-10}$</td>
</tr>
<tr>
<td>423</td>
<td>8.56</td>
<td>$2.00 \times 10^{13}$</td>
<td>$1.10 \times 10^9$</td>
<td>150</td>
<td>$3.29 \times 10^{-10}$</td>
</tr>
<tr>
<td>433</td>
<td>8.78</td>
<td>$1.88 \times 10^{13}$</td>
<td>$6.00 \times 10^{-4}$</td>
<td>50</td>
<td>$5.57 \times 10^{-10}$</td>
</tr>
<tr>
<td>433</td>
<td>8.78</td>
<td>$1.88 \times 10^{13}$</td>
<td>600</td>
<td>100</td>
<td>$5.18 \times 10^{-10}$</td>
</tr>
<tr>
<td>433</td>
<td>8.78</td>
<td>$1.88 \times 10^{13}$</td>
<td>$7.00 \times 10^8$</td>
<td>150</td>
<td>$5.61 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Secondly, the value of $k_s$ nearly doubles upon increasing the temperature by just 10 K (from 423 to 433 K); this temperature dependence would of course be even more significant for temperature variations of, say, 50 – 100 K, and therefore the Arrhenius-type dependence of $k_s$ on T cannot be neglected, as the reaction rate is directly proportional to the $k_s$ value.

Finally, for both temperatures tested in this study, the values of $k_s$ were $\sim 10^{-10}$ s$^{-1}$, so that the estimated magnitude of the Damköhler number would be

$$
Da = \frac{k_s r}{D} \sim \frac{(10^{-10})(10^{-9})}{(10^{-10})} = 10^{-9} \ll 1
$$

(4.24)

Because $Da \ll 1$, the hydrothermal growth of anatase nanoparticles in ethanol can be considered reaction-controlled rather than diffusion-controlled. This qualitative finding allows one to greatly simplify the growth rate expression in Equation (4.15), which in
turn makes it possible to quantitatively determine fundamental kinetic and thermodynamic growth parameters, as will be discussed in the next section.

4.4. Proposed method for estimating thermodynamic and kinetic parameters from initial growth rates

Despite the qualitatively good fits to experimental data afforded by the single-particle growth model, it would be preferable for one to be able to experimentally determine values for parameters such as $k_0$ and $E_a$, instead of assigning them approximate, widely varying, and possibly incorrect values as in the previous section. In this section it will be shown that, under a certain set of assumptions and approximations, it is possible to use the single-particle growth model to extract values of thermodynamic and kinetic parameters from experimental growth data for monodisperse TiO$_2$ dots. In particular, a system of four equations and four unknowns, corresponding to hypothetical growth experiments conducted at four different temperatures, will be used to derive expressions for the surface reaction activation energy $E_a$, the preexponential constant $k_0$, the surface tension $\gamma$, and the solubility $c_\infty$ of an infinite, flat, perfect anatase surface.

First, if one assumes that particle growth is reaction-controlled, i.e., that the Damköhler number is very small, then the denominator of equation (4.15) goes to 1 and the expression simplifies to:

$$\frac{dr}{dt} \approx k_s V_m \left[ c_b - c_\infty \exp \left( \frac{2\gamma V_m}{rRT} \right) \right]$$
\[ = V_m k_0 \exp\left(-\frac{E_a}{RT}\right) \times \left[ c_0 - c_m \exp\left(\frac{2\gamma V_m}{r_0 RT}\right)\right] \]  

(4.25)

The assumption of reaction-controlled growth was qualitatively validated for hydrothermally derived anatase particles in Section 4.3.2, so the expression in equation (4.25) is reasonable. For a given initial concentration \(c_0\) and reaction temperature \(T_i\), the initial rate is:

\[ \frac{dr}{dt}(T_i) \Big|_0 \equiv V_m k_0 \exp\left(-\frac{E_a}{RT_i}\right) \left[ c_0 - c_m \exp\left(\frac{2\gamma V_m}{r_0 RT_i}\right)\right] \]  

(4.26)

To further simplify the determination of approximate values for the activation energy \(E_a\) and the preexponential factor \(k_0\), the analysis shall temporarily be confined to reactions in which the starting concentration is much larger than the size dependent solubility term, i.e.,

\[ c_0 \gg c_m \exp\left(\frac{2\gamma V_m}{r_0 RT_i}\right) \]  

(4.27)

so that the initial rate expression reduces to:

\[ \frac{dr}{dt}(T_i) \Big|_0 = \Gamma(T_i) \Big|_0 \equiv V_m k_0 \exp\left(-\frac{E_a}{RT_i}\right) c_0 \]  

(4.28)
Under these assumptions it is possible, in principle, to determine $E_a$ and $k_0$ by conducting two growth experiments using the same starting concentration but different temperatures $T_1$ and $T_2$, thus generating a system of two equations in two unknowns:

$$r'(T_1)_0 \equiv V_m k_0 \exp \left( \frac{-E_a}{RT_1} \right) c_0$$  \hspace{1cm} (4.29a)$$

$$r'(T_2)_0 \equiv V_m k_0 \exp \left( \frac{-E_a}{RT_2} \right) c_0$$  \hspace{1cm} (4.29b)$$

Division of (4.29a) by (4.29b) followed by rearrangement of terms yields the following expression for the activation energy:

$$E_a = \frac{RT_1 T_2}{T_1 - T_2} \ln \frac{r'(T_1)_0}{r'(T_2)_0}$$  \hspace{1cm} (4.30)$$

Then, substituting (4.30) into (4.29a) and solving for $k_0$, one obtains:

$$k_0 = (V_m c_0)^{-1} \times [r'(T_1)_0]^{-(T_2 - T_1)/T_1} \times [r'(T_2)_0]^{T_2 / (T_2 - T_1)}$$  \hspace{1cm} (4.31)$$

Having calculated the values of $E_a$ and $k_0$, one may now determine the remaining unknowns $\gamma$ and $c_\infty$ using another set of two equations and two unknowns. Reintroducing $\gamma$ and $c_\infty$ into the problem requires relaxation of the earlier assumption that $c_0 >> c_\infty$
exp(2V_mγ / rRT), so that the analysis now includes situations in which the initial bulk concentration is significantly lower than in the hypothetical experiments used for estimating $E_a$ and $k_0$. The following equations will therefore use the term $c_{0.2}$ to denote a smaller initial bulk concentration than before.

The system of two equations and two unknowns necessary for deriving expressions for $\gamma$ and $c_\infty$ corresponds to two new hypothetical experiments, conducted at temperatures $T_3$ and $T_4$ such that $T_1 \neq T_2 \neq T_3 \neq T_4$. Then

\[
r'(T_3)_i \equiv V_m k_0 \exp \left( \frac{-E_s}{RT_3} \right) c_{0.2}
\]

\[
r'(T_4)_i \equiv V_m k_0 \exp \left( \frac{-E_s}{RT_4} \right) c_{0.2}
\]

Rearrangement of (4.32a) yields an expression for $c_\infty$:

\[
c_\infty \equiv \exp \left( \frac{-\varepsilon \gamma}{T_3} \right) \times c_{0.2} - \left( V_m k_0 \right)^{-1} \times r'(T_3)_i \times \exp \left( \frac{E_s}{RT_3} \right)
\]

where $\varepsilon = 2V_m / r_0 R$. Next, substituting (4.33) into (4.32b) and solving for the surface tension, one obtains:
\[
\gamma \equiv \frac{T_3 T_4}{\varepsilon (T_3 - T_4)} \ln \left\{ \frac{c_{0,2} - \left[ (V_m k_0)^{-1} \times r' (T_3) \right]_0 \times \exp \left( \frac{E_\varepsilon}{RT_3} \right)}{c_{0,2} - \left[ (V_m k_0)^{-1} \times r' (T_4) \right]_0 \times \exp \left( \frac{E_\varepsilon}{RT_4} \right)} \right\} \tag{4.34}
\]

Finally, substitution of (4.34) into (4.33) gives an equation for the solubility of an infinite, perfect surface in terms of known quantities:

\[
c_\infty \equiv c_{0,2} - (V_m k_0)^{-1} \times r' (T_3)_0 \times \exp \left( \frac{E_\varepsilon}{RT_3} \right)^{-T_3/(T_4 - T_3)} \times \left[ c_{0,2} - (V_m k_0)^{-1} \times r' (T_4)_0 \times \exp \left( \frac{E_\varepsilon}{RT_4} \right)^{-T_4/(T_4 - T_3)} \right] \tag{4.35}
\]

This analysis has not yet been applied to actual experiments but could readily be tested by running four hydrothermal anatase syntheses, each at a different temperature, and withdrawing aliquots to create a growth curve as described in Section 4.3.2.

4.5. **Summary and future work**

The single-particle growth model offers both a quick, convenient way to qualitatively estimate surface reaction parameters for anatase nanoparticle growth and, for the first time, a quantitative method for determining fundamental kinetic and thermodynamic quantities for monodisperse nanoparticle systems in which growth is reaction-controlled. There are, however, limitations to this model’s validity: it only
applies to monodisperse systems i.e., it does not treat size distributions; it is limited to isotropic (spherical) particle morphologies; it does not model nucleation, either before or at the same time as particle growth; it requires one to assume a value for the initial radius $r_0$ that may or may not be correct; and the analysis in Section 4.4, whereby kinetic and thermodynamic parameters are estimated, is invalid for systems characterized by diffusion-controlled growth.

Possible future studies incorporating the present model include the following: applying the single-particle growth scheme to other monodisperse nanoparticle systems, especially CdSe, for which similar models neglecting the Arrhenius dependence of the surface reaction rate have already been evaluated and would therefore provide a useful comparison for the analysis described here; seeded growth studies, i.e., growth of new material onto existing particles whose radius has been experimentally determined, so that one can assign a known value of $r_0$ in the simulations; incorporation of crystal size distributions, and thus a distribution of growth rates, into the model; and simultaneous treatment of growth and nucleation, so as to more accurately simulate real nanoparticle growth.

References


Chapter 5

Literature review II: Heterogeneous photocatalysis with titanium dioxide

5.1. Introduction

One of the most frequently studied and environmentally significant applications of nanocrystalline titanium dioxide is heterogeneous photocatalysis, i.e., light-induced chemical transformations of gas- or solution-phase species on the surface of a solid catalyst, usually a semiconductor. The first indication that TiO$_2$ might be a powerful photocatalyst for environmental applications came in 1971, when Fujishima and Honda used a TiO$_2$ electrode to photochemically cleave water and produce hydrogen gas.$^1$ This process is, if anything, even more important today, as the potential advantages of switching from fossil fuels to a hydrogen-based fuel economy become more apparent with each passing year, and during the last thirty years there have been numerous studies devoted to optimization of photoelectrochemical water cleavage with TiO$_2$-based catalysts.$^{2-12}$ Meanwhile researchers have explored a variety of other TiO$_2$-catalyzed photoinduced transformations of environmental and/or biological interest, including oxidation of CO,$^{13}$ degradation of NO and NO$_2$,$^{14,15}$ inactivation of bacteria,$^{16-18}$ and destruction of cancer cells.$^{19}$

Perhaps the most significant photocatalytic application for TiO$_2$, however, is the photooxidative degradation of organic species in the air and in wastewater systems. TiO$_2$ is generally recognized as the best semiconductor photocatalyst for oxidative remediation of water contaminated by organics,$^{20}$ and literally hundreds of studies have been done on TiO$_2$-mediated destruction of harmful or recalcitrant organic pollutants such as
polychlorobiphenyls (PCBs),\textsuperscript{21} toluene,\textsuperscript{22-25} surfactants,\textsuperscript{26} pesticides and pesticide precursors,\textsuperscript{27-32} herbicides,\textsuperscript{33} phenols and phenolic compounds,\textsuperscript{30,34-44} carboxylic acids,\textsuperscript{45-49} halogenated hydrocarbons,\textsuperscript{50-57} aromatic sulfides,\textsuperscript{58} and dyes.\textsuperscript{30,59-65} In some cases the contaminant molecule is only partially oxidized to an innocuous or less harmful species, while in other cases photocatalytic oxidation results in complete mineralization, i.e., the pollutant is completely converted to CO\textsubscript{2}, H\textsubscript{2}O, and other small inorganic molecules.\textsuperscript{66}

Given the enormous variety of organic compounds that can be partially or completely destroyed by TiO\textsubscript{2}-mediated photooxidation, there has naturally been a great deal of interest in finding ways to improve the efficiency of TiO\textsubscript{2} photocatalysts. Certainly the efficacy of a photocatalyst will depend in part on the specific reaction being studied as well as on the exact reaction conditions (e.g., temperature, pH, presence or absence of O\textsubscript{2}, and degree of substrate adsorption to the catalyst surface), but it is also important to be able to design the photocatalyst itself to have physical properties that will maximize its catalytic activity for a variety of reactions.

This latter problem of optimizing a material’s photocatalytic behavior has attracted a great deal of attention in recent years, and several factors have been identified as possible determinants of a TiO\textsubscript{2} photocatalyst’s activity, including grain size, surface area, phase composition, defect sites, extent of surface hydroxylation, and surface modifications. However, the relative importance of each of these factors is not always clear, nor, in many cases, is the exact nature of a given physical property’s influence over photocatalytic efficiency. For instance, contradictory and/or ambiguous results have been published regarding the effect of a TiO\textsubscript{2} sample’s crystalline structure on its activity; although the anatase phase is usually regarded as a superior photocatalyst to the rutile
phase,\textsuperscript{10,20,67-70} there have been some reports in which rutile has exhibited activities comparable to\textsuperscript{71-74} or even greater than\textsuperscript{11,66,75} those of anatase. Some of this variability in the relative efficiencies of the two phases is undoubtedly attributable to the different reactions and conditions involved in different studies; however, one must also take into account that each titania sample possesses a unique set of physical characteristics, and that the photocatalytic activity of the sample depends upon the combined, sometimes competing effects of these physical properties. It is also worth noting that most researchers report the photocatalytic activities of titania samples on a per gram basis, i.e., without normalizing the results to the available surface area; as a result, it is not always clear whether, for example, an anatase sample performs better than a rutile sample because of differences in crystalline structure or because the anatase sample has a higher specific surface area (surface area per gram).

Considering the importance of maximizing the efficiency of TiO\textsubscript{2} photocatalysts, one of the goals of the present work was to clarify fundamentally how, to what extent, and under what circumstances a TiO\textsubscript{2} sample’s various physical properties affected its performance. The purpose of this chapter is to provide an overview of the physical characteristics of TiO\textsubscript{2} that determine photocatalytic activity, along with a summary of insights from the existing literature regarding the specific effects of these factors. Because the current work is concerned primarily with photocatalysis as a means of degrading organic species in water, a process that almost always involves oxidative reactions, the discussions in this chapter will be limited to principles and experiments related to photooxidation. Furthermore, since only pure TiO\textsubscript{2} catalysts were studied in the present work, only a brief section on doping and other surface modifications is included.
in this review. For a more comprehensive discussion of the different kinds of photocatalytic reactions (both oxidative and non-oxidative) that have been carried out in the presence of TiO$_2$, as well as the types of surface modifications that have been found to improve catalytic performance, the reader is referred to the reviews by Fox and Dulay,$^{20}$ Linsebigler et al.,$^{69}$ and Hoffmann et al.$^{66}$

5.2. Basic principles of TiO$_2$-mediated photooxidation in aqueous solutions

5.2.1. Steps in photocatalytic oxidation reactions

To understand how and why the physical characteristics of TiO$_2$ influence its efficiency in photocatalytic oxidation reactions, it is necessary to first understand what takes place during these reactions at the molecular level. Figure 5.1 schematically illustrates the events involved in a typical TiO$_2$-mediated photooxidation of an organic species (denoted $A$) in an aqueous environment. First, the $A$ molecules (the adsorbates) are reversibly adsorbed (i.e., attached via electrostatic or chemical forces) to the TiO$_2$ surface (the adsorbent):

$$A \rightarrow A\text{ (ads)} \quad (5.1)$$

Depending on the adsorbate and the TiO$_2$ sample, adsorption equilibrium may be established after as little as an hour or as long as several days. Several authors have noted that adsorption of the reactants to the TiO$_2$ surface prior to irradiation in photocatalysis is essential for efficient photooxidation, which suggests that TiO$_2$-mediated photocatalytic
Figure 5.1. Schematic representation of the elementary steps in TiO$_2$-mediated photooxidation.

(a) $e^-/h^+$ recombination (red arrows) or (b) reduction of adsorbed O$_2$ (blue arrows)
(b) oxidation of A to B by (a) valence band holes (red arrows) or (b) trapped holes (e.g., as OH$^-$)

Reactions are indeed dominated by processes that occur on the semiconductor particles' surfaces rather than between free species in solution.$^{20,66,68,69}$

Next, the aqueous suspension of TiO$_2$ + adsorbate is irradiated with ultraviolet light of energy $E_{hv}$ equal to or greater than the TiO$_2$ sample's band gap energy $E_g$, resulting in the promotion of a valence band (VB) electron to the conduction band (CB). This photoexcitation results in the creation of an electron/hole ($e^-/h^+$) pair, the lifetime of which is a critical determinant of a photocatalyst's efficiency.
\[ hv + \text{TiO}_2 \rightarrow \text{TiO}_2 + e^- + h^+ \]  \hspace{1cm} (5.2)

The excited electron can either recombine with the hole or go on to reduce an adsorbed electron acceptor, most likely molecular oxygen:\textsuperscript{20,69,76,77}

\[ e^- + h^+ \rightarrow \text{heat} \]  \hspace{1cm} (5.3a)

\[ e^- + \text{O}_2 \text{ (ads)} \rightarrow \text{O}_2^{*\ast} \text{ (ads)} \]  \hspace{1cm} (5.3b)

In the absence of electron- or hole-trapping species on the TiO\textsubscript{2} surface, e\textsuperscript{-}/h\textsuperscript{+} recombination will occur within 10-100 ns. The reduction of surface adsorbed oxygen, on the other hand, is a much slower process that requires 1 ms or longer; many investigators, in fact, regard O\textsubscript{2} reduction as the rate determining step in photocatalytic destruction of organics.\textsuperscript{69,78,79} In order for the CB electron to participate in the reduction of O\textsubscript{2} or another electron acceptor on the surface, e\textsuperscript{-}/h\textsuperscript{+} recombination must be inhibited via the trapping of electrons and/or holes in thermodynamically favorable states, designated e\textsubscript{t} and h\textsubscript{t} respectively, between the VB and CB as shown in Figure 5.2. According to Hoffmann et al., charge carrier trapping can occur either in the presence of a surface adsorbed charge scavenger (e.g., hole trapping by surface hydroxyls, the time scale for which is \( \sim 10 \) ns) or at a surface defect site (e.g., electron trapping at a coordinatively unsaturated Ti\textsuperscript{4+} to produce Ti\textsuperscript{3+}, which also occurs within \( \sim 10 \) ns).\textsuperscript{66} It is important to note that in order to compete with the very rapid process of e\textsuperscript{-}/h\textsuperscript{+} recombination, the charge traps must be readily accessible to photogenerated electrons and holes, i.e., the
charge scavengers and/or defect sites must be located either at the surface or within the volume of the TiO₂ particle bearing the adsorbate A. This is why it is essential for not only A but also any electron- or hole-scavenging species to be preadsorbed to the semiconductor surface; otherwise, e⁻/h⁺ recombination would take place long before the charge carriers could migrate to the vicinity of either charge trapping sites or the surface sites occupied by A molecules.

If the condition of charge carrier trapping is met, then the photogenerated hole will have sufficient time to initiate oxidative degradation of A to some other species B. In principle there are two ways in which this oxidation can occur: direct hole attack, in which the (untrapped) VB hole itself reacts with A to produce B (equation 5.4), or hydroxyl-mediated attack, in which the hole reacts with (is trapped by) a surface adsorbed hydroxyl group to produce a reactive radical (most likely OH⁺) which then oxidizes A to B (equations 5.5a and 5.5b).

\[ h^+ + A \text{ (ads)} \rightarrow B \text{ (ads)} \quad (5.4) \]

\[ h^+ + OH^- \text{ (ads)} \rightarrow OH^+ \text{ (ads)} \quad (5.5a) \]

\[ OH^+ \text{ (ads)} + A \text{ (ads)} \rightarrow B \text{ (ads)} \quad (5.5b) \]

These interfacial charge transfer reactions, in which the actual adsorbate destruction occurs, typically require times of 100 ns; again, this time scale is comparable to or even slower than charge carrier recombination, and therefore the trapping of photogenerated electrons and/or holes is a necessary condition for the efficient photooxidation of A.
Finally, once \( A \) has been chemically converted to \( B \), the latter desorbs from the TiO\(_2\) surface and diffuses into solution:

\[
B \text{ (ads)} \rightarrow B \tag{5.6}
\]

It should be noted that depending on the chemical nature of \( A \) and \( B \) (as well as the nature of the surface sites they occupy), the time scales for their adsorption and desorption can vary greatly, which in turn can affect how efficiently the photocatalytic conversion of \( A \) to \( B \) takes place. If, for instance, \( A \) adsorbs only weakly to the TiO\(_2\) surface, it follows that the probability of direct or indirect oxidation of \( A \) on the surface (and thus the efficiency of the photocatalytic reaction) will be low. Likewise, if the oxidation product \( B \) is slow to desorb from a surface site, then other \( A \) molecules will be prevented from accessing that site and the conversion efficiency for \( A \rightarrow B \) will be reduced.

### 5.2.2. Nature of the oxidant

Despite the apparent simplicity of the photocatalytic reaction steps outlined in Section 5.2.1, there exists some controversy regarding the exact nature of the events that occur after the light-induced generation of the \( e^-/h^+ \) pair. In particular, researchers do not always agree on which species is primarily responsible for the oxidation of adsorbed organics. It appears that most investigators believe surface OH\(^+\) radicals, resulting from reaction between photogenerated holes and surface hydroxyl groups (equation 5.5a), to be the primary oxidants in photocatalysis.\(^{69}\) Evidence for OH\(^+\) as the main photooxidant includes the observation of hydroxylated intermediates during the photodegradation of
organics;\textsuperscript{37,40,52,80,81} transient absorption and emission spectra as well as electron spin resonance (ESR) studies that indicate trapping of photogenerated holes by OH\textsuperscript{-} groups on TiO\textsubscript{2} surfaces;\textsuperscript{2,82-84} the improved photocatalytic performance of both anatase and rutile when the number of surface hydroxyls is large;\textsuperscript{35,40,85} and, most recently, an observed linear relationship between the concentration of surface OH\textsuperscript{*} radicals and the biocidal activity of TiO\textsubscript{2} in the photocatalytic inactivation of \textit{E. coli}.\textsuperscript{17} In 2000 El-Morsi et al.\textsuperscript{53} clarified that it is indeed surface adsorbed OH\textsuperscript{*} radicals, and not free OH\textsuperscript{*} in solution, that are responsible for oxidation of organic species in TiO\textsubscript{2}-mediated photocatalysis; during the photodegradation of 1,10-dichlorodecane in an aqueous suspension of TiO\textsubscript{2}, the investigators noted that addition of tetranitromethane, a known scavenger of free OH\textsuperscript{*} radicals, had essentially no effect on the degradation rate, indicating that the oxidation of the chlorinated hydrocarbon involved exclusively surface adsorbed species.

Yet for all the evidence pointing to the importance of OH\textsuperscript{*} radicals in photocatalytic oxidations, it is still possible that other oxidizing species play a competing or even dominant role in these reactions. Micic et al.,\textsuperscript{86} for instance, found evidence in a 1993 electron paramagnetic resonance (EPR) study that the primary oxidant in TiO\textsubscript{2}-assisted photodecomposition of an aqueous methanol solution is either the photogenerated hole itself or a surface oxygen radical, \textsuperscript{=Ti—O\textsuperscript{*}}, that results from hole attack on adsorbed hydroxyl groups. (It should be noted that, in the latter case, the presence of surface hydroxyls would still be essential for efficient photooxidation.) More recently, Kapinus et al.\textsuperscript{65} proposed that the O\textsubscript{2}\textsuperscript{*} radical formed via reduction of adsorbed O\textsubscript{2} by a photogenerated electron (equation 5.3b) could serve as an oxidizing species in addition to, or instead of, OH\textsuperscript{*}. Still other studies have reported that in some
photocatalytic reactions, direct oxidation by a photogenerated valence-band (VB) hole (i.e., a hole that is not trapped by a surface adsorbed species such as OH\(^{-}\)) may be favored over indirect oxidation by OH\(^{-}\) or other surface radicals in the case of both TiO\(_2\) and other semiconductors such as ZnO.\(^{87,88}\) Finally, it is possible that both direct hole oxidation and indirect, surface species-mediated oxidation occur simultaneously.\(^{89}\)

As is the case with many observations of photocatalytic systems, one reason for contradictory evidence regarding the primary oxidant in heterogeneous photocatalysis may be that different reactions proceed according to different oxidation pathways. Additionally, the structural and surface properties of the TiO\(_2\) catalyst being studied will play a role in determining the reaction mechanism. Most of the time, researchers studying photocatalysis assume OH\(^{-}\) as the primary oxidant, and in the majority of these cases such an assumption has been consistent with experimental results. Nevertheless, as other studies have made clear, one must always be prepared to modify or even discard any presuppositions regarding the nature of photocatalytic oxidation, particularly when it comes to designing a photocatalyst surface to be optimized for a given reaction. In some cases it may be advantageous to maximize surface hydroxylation, while for other reactions the opposite may be true.

In spite of the ambiguities discussed above, however, it is clear that at least two conditions must be met in order for photocatalytic oxidation to proceed efficiently: First, as previously mentioned in Section 5.2.1, the reactant molecules must be adsorbed to the surface of the catalyst; and second, the recombination of photogenerated electrons and holes must be inhibited so that the charge carriers are available for the surface redox reactions enumerated in equations 5.3b, 5.4, 5.5a, and 5.5b. As will be shown in the next
section, the dependence of a photocatalyst’s activity on its physical properties can be best understood in terms of how such properties influence the two critical phenomena of adsorption and charge separation.

5.3. Factors affecting the photocatalytic activity of TiO₂

5.3.1. Surface area, grain size, and agglomeration

Since heterogeneous photocatalysis takes place on solid particle surfaces, the efficiency of any photocatalytic reaction will depend in part on the total surface area available for adsorption. It is therefore desirable to produce TiO₂ photocatalyst powders or films consisting of unagglomerated, ultrafine (nanoscale) particles so as to maximize the surface area per gram of material. As mentioned in Chapter 2, several strategies exist for minimizing both the grain size and the degree of agglomeration in TiO₂ nanocrystals; one such technique is peptization of a TiO₂ colloid with an acid or surfactant that stabilizes particle surfaces against growth and/or agglomeration.

However, as has already been seen, adsorption is not the only phenomenon to consider when optimizing photocatalytic efficiency; one must also take into account whether and how a given physical property affects charge carrier separation and recombination and other, related electronic properties. In the case of grain size, it is not entirely clear whether a decrease in crystallite dimensions affects charge carrier dynamics in a way that tends to increase or decrease photocatalytic activity. In particular there has been disagreement over whether size quantization effects, i.e., effects arising from the quantum confinement of charge carriers in ultrafine particles less than \( \sim 10 \) nm in
diameter ("Q-particles"), would promote or inhibit $e^-/h^+$ recombination. On the one hand, when an $e^-/h^+$ pair is confined to a small volume (i.e., a small particle), the likelihood of recombination is high because the two charges are close together; on the other hand, electrons and/or holes can more easily migrate to the surface and access charge-trapping sites in small particles than in large ones.

Further complicating matters is the fact that size quantization in semiconductors results in an increase in the energy level of the conduction band (CB), which again could either degrade or improve a material’s photocatalytic performance. Since the CB energy increases while the valence band (VB) energy remains the same, it follows that the total band gap energy $E_g$ is larger for a Q-particle than for larger particles, the consequence of which is that the material absorbs light less efficiently and might therefore perform less effectively as a photocatalyst. However, by the same token, a CB energy increase results in an increase in the redox potential for reactions at the semiconductor surface – in particular, the reduction of molecular oxygen by CB electrons – so there is a greater energetic driving force for at least one of the elementary reactions essential for efficient photocatalysis.

Given the numerous competing and/or complementary effects observed in very fine semiconductor particles – increased surface area, proximity of charge carriers both to each other and to surface trapping sites, and energetic effects related to the blue shift in CB energy that results from quantum confinement of charges – it is reasonable to expect that there exists an optimum particle size for which a material’s photocatalytic efficiency is at a maximum. Such an optimum dimension (denoted in this review as $D^*$) has indeed been identified experimentally in a number of studies on both gas- and solution-phase
photocatalysis with TiO₂, though the exact D* values vary from reaction to reaction and from sample to sample. Wang et al.⁵⁷ have reported a D* of 11 nm for the photodegradation of aqueous chloroform by hydrothermally prepared anatase nanoparticles; Cao et al.⁹⁰ have identified D* = 5 – 6 nm as the optimal grain size for the gas-phase photooxidation of 1-butene over anatase obtained in an acidic sol-gel synthesis; and Almquist and Biswas⁴² have found that D* lies in the range 25 – 40 nm for phenol decomposition using TiO₂ samples prepared by flame pyrolysis. Based on these studies it is difficult to say whether the optimal grain size depends more on the reaction or on the preparation method, but it is at least qualitatively apparent that the photocatalytic activity of TiO₂ can be optimized by tuning the crystallite size, which essentially amounts to tuning both the surface properties and the electronic properties of the material.

5.3.2. Crystallinity and phase composition

It is generally agreed that in order for a TiO₂ sample to serve as an efficient photocatalyst, it must possess a high degree of crystallinity, i.e., the amorphous content must be either zero or negligible. More controversial, however, is the question of which TiO₂ polymorph – anatase, rutile, or brookite – is best suited for photocatalytic reactions. As briefly discussed in Section 5.1, most researchers consider anatase to be by far the best photocatalyst of the three major phases,¹⁰,²⁰,⁶⁷-⁷⁰ but for certain photocatalytic reactions and/or under certain environmental conditions rutile can compete with⁷¹-⁷⁴ or even outperform¹¹,⁶⁶,⁷⁵ anatase. Brookite, although seldom studied in a photocatalytic context, has likewise been shown to be highly active in certain aqueous photocatalytic
redox reactions, such as dehydrogenation of isopropanol and silver metal deposition from silver salt solutions. 

Clearly it is impossible to identify a single TiO$_2$ polymorph that can be expected to be a superior photocatalyst under all conceivable circumstances. Nevertheless, by examining the electronic, structural, and surface properties of each phase, one can obtain some insight as to the advantages and disadvantages each polymorph possesses in photocatalysis. The next two sections are therefore devoted to a discussion of molecular-level properties of phase-pure (Section 5.3.2.1) and mixed-phase TiO$_2$ catalysts (Section 5.3.2.2). Because of the scarcity of photocatalytic data on brookite, the discussion of phase composition effects in this chapter will focus mostly on the anatase and rutile polymorphs.

5.3.2.1. Phase-pure TiO$_2$ catalysts: anatase versus rutile

Hurum et al.\textsuperscript{94} recently enumerated the major structural, electronic, and surface properties affecting the photocatalytic activity of anatase and rutile; these characteristics are summarized in Table 5.1. Examination of the properties of each phase reveals that there are competing contributions from various physical characteristics to the overall photocatalytic activity in both anatase and rutile.

5.3.2.1.1. Band gap energies

Bulk anatase has a band gap energy of $E_g = 3.2$ eV, which corresponds to an excitation wavelength of $\lambda = 385$ nm; the band gap energy of bulk rutile, on the other hand, is slightly smaller ($E_g = 3.0$ eV, $\lambda = 410$ nm), which means rutile has a greater
Table 5.1. Summary of physical properties that influence the photocatalytic activities of anatase- and rutile-phase TiO₂. (Information obtained from Hurum et al., Journal of Physical Chemistry B, 2003, 107, 4545.)

<table>
<thead>
<tr>
<th>Property</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of commercially available particles (nm)</td>
<td>&lt; 50</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>Band gap energy (bulk scale) (eV)</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Maximum excitation wavelength (nm)</td>
<td>385</td>
<td>410</td>
</tr>
<tr>
<td>Adsorptive affinity for organics</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Relative hole trapping rate</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

range of UV light absorption than anatase at the bulk scale. (The band gap energy for brookite, incidentally, was only recently experimentally measured; the value obtained was approximately 3.4 eV and was derived from optical measurements on 10 nm brookite crystallites, for which size quantization effects may or may not have been significant.⁹⁵)

What happens, though, at particle sizes smaller than 10 nm, where size quantization effects become important? For very small TiO₂ particles, both anatase and rutile should exhibit a blue shift (i.e., an increase) in their band gap energies; such a shift can be estimated using the approximation proposed by Wang and Herron:⁹⁶

\[
\Delta E_g = \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e} + \frac{1}{m_h}\right) - 1.786 \frac{e^2}{\epsilon r} - 0.248E_{Ry}^* \tag{5.7}
\]

where \(\Delta E_g\) is the band gap shift; \(\hbar\) is Planck’s constant, equal to \(1.1 \times 10^{-34}\) J s; \(r\) is the particle radius in meters; \(m_e\) and \(m_h\) are the respective effective masses of the electron and hole in a photogenerated \(e^-/h^+\) pair; \(e\) is the elementary unit of charge (\(1.6 \times 10^{-19}\) C);
\( \varepsilon \) is the dielectric constant of the TiO\(_2\) photocatalyst (48 for anatase, 114 for rutile);\(^{97}\) and \( E_{RY}^* \) is the effective Rydberg energy, given by

\[
E_{RY}^* = \frac{e^4}{2\varepsilon^2\hbar^2 \left( \frac{1}{m_e} + \frac{1}{m_h} \right)}
\]

(5.8)

Although Wang and Herron caution that the band gap shifts calculated by equation 5.7 are not always found to be quantitatively accurate in experimental studies, the equation is at least qualitatively correct in predicting shifts to be on the order of a few tenths of an eV for TiO\(_2\) particles less than 10 nm in diameter.\(^{98}\) In any case, it should be noted that even when size dependent band gap shifts are taken into account, rutile is still expected to have a smaller \( E_g \) than anatase; this is because the second and third terms of equation 5.7, which depend on the different dielectric constants of anatase and rutile, are usually very small compared with the first, phase-independent term, so that the magnitudes of \( \Delta E_g \) for identically sized anatase and rutile nanoparticles should be comparable.

On the basis of band gap size alone, then, one might expect rutile to be a more efficient photocatalyst than anatase both at the bulk scale and at the nanometer scale. Yet as has already been mentioned, the reverse is usually true. It is therefore evident that other factors are responsible for the relative photocatalytic activities of the two phases.

5.3.2.1.2. Charge carrier dynamics and redox potentials

In the discussion of size quantization effects in Section 5.3.1, it was pointed out that the size of a semiconductor photocatalyst's band gap influenced not only the
material’s light absorption properties but also the energetic driving force for the reduction of surface adsorbed O₂ molecules by CB electrons; as Tanaka et al. have noted, the CB of anatase is “sufficiently negative for the reduction of oxygen, whereas that of rutile is [so] close to the oxygen reduction potential” that O₂ reduction in rutile may be too slow to compete effectively with e⁻/h⁺ recombination, which would preclude the participation of holes in oxidative processes on the rutile surfaces. Whether or not size quantization is applicable, the simultaneous, competing effects of less efficient light absorption and more energetically favorable redox processes associated with larger band gaps are important in determining the relative photocatalytic efficiencies of anatase and rutile. Given the usually superior photocatalytic performance of anatase, it is likely that the latter effect – a larger redox potential resulting from anatase’s larger band gap – is ultimately more important than anatase’s smaller range of UV light absorption (λ < 385 nm) relative to that of rutile (λ < 410 nm).

In addition to its more favorable redox properties, anatase has a significantly higher hole trapping efficiency than rutile. Again, the consequence of this is that e⁻/h⁺ recombination is inhibited far more effectively in anatase, which helps to explain its generally higher activity.

5.3.2.1.3. Typical grain sizes and surface properties

As shown in Table 5.1, the typical grain sizes and surface properties of anatase and rutile are quite different. Among commercially available nanocrystalline TiO₂ powders, the anatase samples usually have average grain sizes of 50 nm or less, while rutile grain sizes are rarely less than 200 nm. Likewise, homemade anatase nanopowders
typically exhibit smaller grain sizes than homemade rutile. One reason for this large difference in typical crystallite sizes of the two phases is that rutile, which is the thermodynamically stable phase of TiO$_2$ at the bulk scale, actually becomes less thermodynamically stable than anatase for grain sizes less than \( \sim 11 \) nm;\textsuperscript{99} it is therefore far more difficult to prepare ultrafine rutile than ultrafine anatase.

Because rutile generally consists of larger particles than anatase, the specific surface areas of the former phase are usually much smaller than those of the latter. This difference in surface area, combined with the fact that anatase has a higher adsorptive affinity for organics than rutile, could partially account for the higher photocatalytic efficiencies typically observed in anatase; the greater the extent of contaminant adsorption to a TiO$_2$ surface, the better the photocatalyst should perform. Indeed, Kim et al.\textsuperscript{91} recently found that when rutile is prepared in rodlike form with particle widths of 3 – 7 nm and correspondingly high specific surface areas, the material performs better than commercially available TiO$_2$ in the photocatalytic removal of metal ions from aqueous solutions.

Again, however, one must consider that photocatalytic activities are often reported on a per gram basis, so that it is not always clear whether one phase performs better than another because of surface area differences or because of some other effects related to fundamental structural and electronic properties. On occasion, researchers have attempted to clarify this matter by normalizing photoactivity results to unit surface area, i.e., by reporting “specific activities,” as Ku et al.\textsuperscript{73} did for the photocatalytic degradation of aqueous 2-chlorophenyl; in that experiment, the investigators found that anatase is more efficient than rutile on a per gram basis, but that the two phases have similar
efficiencies on a per surface area basis. Nevertheless, this does not necessarily mean anatase and rutile will always exhibit comparable specific activities; efficiencies will also depend on both the reaction and physical properties other than surface area.

5.3.2.2. Mixed-phase TiO$_2$ photocatalysts

Considering the generally poor photocatalytic properties of rutile, one might expect the incorporation of rutile into an anatase sample would have a deleterious effect on the photocatalytic activity, but in fact numerous studies on both commercial and homemade nano-TiO$_2$ have revealed that the opposite is often true; that is, there appears to be a synergy between anatase and rutile in mixed-phase TiO$_2$ samples that enhances photocatalytic performance, almost certainly by enhancing charge separation after photoinduced formation of e$^-$/h$^+$ pairs.$^{32,33,49,94,100-103}$

The exact mechanism by which this charge separation takes place has been the subject of some controversy in recent years. The original model for e$^-$/h$^+$ separation in mixed-phase nano-TiO$_2$, proposed by Bickley et al.$^{100}$ in a 1991 study of the commercial anatase-rutile mixture P25 (Degussa Corporation), postulated that photoexcitation occurs in anatase while rutile serves as an electron sink, leaving the photogenerated valence-band holes free to access trapping sites at the surface; this model is schematically illustrated in Figure 5.2a. The theoretical basis for such a mechanism is that rutile’s CB has a lower energy than that of anatase, so that it would be energetically favorable for photogenerated electrons to migrate from the anatase CB to the rutile CB. However, this explanation fails to account for electron trapping sites either at the surface or within the volume of the anatase particle, sites that occupy even lower energy levels than that of the
rutile CB and would therefore be more likely to act as electron sinks than a nearby rutile particle.\textsuperscript{94}

A year ago, Hurum et al.\textsuperscript{94} conducted an EPR study on Degussa P25, the results of which suggest an alternative explanation for the observed synergy between anatase and rutile. The EPR data indicate that, once an $e^-/h^+$ is generated in P25 by UV illumination, electrons are transferred from the rutile CB to low-lying trapping states in anatase; in other words, photoexcitation appears to take place in the rutile particles, while anatase serves as the electron sink and holes migrate to lattice or surface trapping sites in the rutile particle where the $e^-/h^+$ was first created. The holes can then either directly or indirectly oxidize contaminant molecules adsorbed on the rutile surface. Meanwhile, the electrons that have been transferred to anatase can migrate to the anatase surface and reduce adsorbed oxygen (or some other electron acceptor). Thus, as illustrated in Figures 5.2b and 5.2c, the presence of both anatase and rutile in a nanocrystalline TiO$_2$ sample results in an enhanced photoactivity in two ways: first, rutile, which has a smaller band gap than anatase, allows the mixed-phase TiO$_2$ to absorb light over a greater range of wavelengths than phase-pure anatase; and second, the presence of energetically favorable electron trapping sites in anatase facilitates the transfer of photogenerated electrons from rutile to anatase, thus inhibiting $e^-/h^+$ recombination.

Hurum et al. noted that in order for their proposed synergistic mechanism to substantially improve the photocatalytic activity of an anatase-rutile mixture over that of phase-pure TiO$_2$, the anatase and rutile particles in mixed-phase TiO$_2$ must be in close contact with one another, and the rutile crystallites must be sufficiently small for photogenerated electrons to migrate across the volume of a rutile particle and access an
Figure 5.2. Proposed mechanisms for charge separation in anatase-rutile mixtures: (a) anatase absorbs light while rutile serves as an electron sink; (b, c) rutile absorbs light while anatase serves as an electron sink. (Figure adapted from Hurum et al., *Journal of Physical Chemistry B*, 2003, 107, 4545.)
adjacent anatase particle before $e^-/h^+$ recombination can occur. Both of these criteria – proximity and small particle size – are met in Degussa P25 powder, as confirmed in electron microscopic studies by Datye et al.\textsuperscript{104} and Ohno et al.\textsuperscript{32} In laboratory-synthesized anatase-rutile mixtures, of course, both the particle interfaces and the crystallite sizes, and consequently the photocatalytic activity, will depend upon the preparation method. Indeed, there have been some reports of homemade anatase-rutile mixtures for which synergistic effects appear to be negligible,\textsuperscript{65,105} and in at least one case mixed-phase TiO$_2$ has actually exhibited a lower activity than pure anatase.\textsuperscript{15}

Additionally, the efficacy of mixed-phase TiO$_2$ photocatalysts may depend on the relative amounts of anatase and rutile. For instance, Ding et al.\textsuperscript{41} prepared anatase-rutile mixtures with different mass compositions by calcining Degussa P25 at different temperatures and found that the samples with higher anatase:rutile ratios (namely, those calcined at lower temperatures so that conversion of anatase to rutile was minimal) tended to perform better as photocatalysts. However, because calcination results not only in grain growth (and thus reduction in surface area) but also in elimination of surface adsorbed OH$^-$ and H$_2$O, the authors cautioned that the decrease in photocatalytic activity with increasing rutile content may not necessarily be related to phase composition. Once again, the influence of crystalline phase over photocatalytic performance is rarely evaluated independent of other factors.

5.3.3. Does nanoparticle shape affect photocatalytic activity?

One question that has not been addressed up until now is whether the shape of the primary particles – and, more specifically, the dominant crystallographic faces in
anisotropic nanocrystals – has any effect on the photocatalytic performance of nanocrystalline TiO2. Kim et al. did suggest that the high activities they observed in rodlike rutile might have been related to the particle shape, but this conclusion was drawn in terms of the very small dimensions (3 – 7 nm) of the minor axis, which probably had the effect of suppressing \( e^-/h^+ \) combination; in other words, the authors did not interpret their results in terms of the possible effects of which crystal faces constituted the majority of the nanoparticles’ available surface area. Furthermore, the study did not test whether the degree of particle anisotropy had any effect on photocatalytic activity.

Studies on other semiconductor photocatalysts have indicated that nanocrystal morphology can indeed enhance or reduce activity depending on which crystallographic faces are predominant. In ZnO, for example, the photocatalytic decomposition of acetaldehyde proceeds more efficiently on the (1 0 -1 0) surface than on the (0 0 0 2) surface. Additionally, while nano-TiO2 has not yet been tested for similar effects, recent theoretical studies of water adsorption to various TiO2 surfaces suggest that certain crystallographic faces may be more photocatalytically active than others depending on whether H2O adsorbs to a surface primarily dissociatively (i.e., as H\(^+\) and OH\(^-\)) or non-dissociatively (i.e., in molecular form). In particular, for the anatase (1 0 1) surface, it is more energetically favorable for H2O to adsorb non-dissociatively than dissociatively, a consequence of which is that there are few OH\(^-\) groups available on this surface for conversion to photocatalytically active OH\(^+\) radicals. By contrast, H2O is more likely to adsorb dissociatively to the anatase (0 0 1) surface, which suggests this surface might be better suited for photocatalytic oxidations in which OH\(^+\) is the primary oxidant. With these considerations in mind, a portion of the present work is dedicated to
determining whether anatase particles in which the (1 0 1) faces are dominant do in fact exhibit reduced activities.

5.3.4. Improving photocatalytic activity through surface modifications.

According to Linsebigler et al.,\textsuperscript{69} there are three ways in which surface modifications can improve the photocatalytic performance of TiO\textsubscript{2}: (1) by suppressing charge carrier recombination, (2) by increasing the range of wavelengths that the photocatalyst can absorb, and (3) by increasing the reaction rate and the product yield. One way to inhibit e\textsuperscript{-}/h\textsuperscript{+} recombination through surface modifications while simultaneously increasing the wavelength response range is to couple TiO\textsubscript{2} to another semiconductor such as RuO\textsubscript{2},\textsuperscript{3,110} SnO\textsubscript{2},\textsuperscript{111,112} or ZrO\textsubscript{2}.\textsuperscript{113} Charge carrier recombination can also be suppressed by doping TiO\textsubscript{2} photocatalysts with transition metal ions such as Fe\textsuperscript{3+},\textsuperscript{114} and Zr\textsuperscript{4+};\textsuperscript{115} however, some transition metal dopants have actually been observed to decrease photocatalytic activity, as is the case with Cr\textsuperscript{3+}.\textsuperscript{69} Meanwhile, dye sensitization has proven to be an effective way to widen the wavelength response range in TiO\textsubscript{2} catalysts,\textsuperscript{6,69,110,116} while deposition of noble metals such as Pt or Au is a common strategy for increasing the reaction rate and/or product yield in photocatalytic reactions.\textsuperscript{69,117} Sheng et al. have also argued that Pt addition improves the photocatalytic activity of TiO\textsubscript{2} by increasing charge separation.\textsuperscript{118}

5.4. Summary and relevance to present work

Over the last three decades, an enormous amount of research has been devoted to understanding, evaluating, and improving the photocatalytic properties of TiO\textsubscript{2}. The
activity of a TiO\textsubscript{2} photocatalyst has been found to depend on physical properties such as grain size, specific surface area, degree of agglomeration, phase composition, and crystallinity; however, contradictory results have been obtained regarding the effects of such properties on photocatalytic performance, partly because activities are reaction- and environment-dependent and partly because different properties are not always evaluated independent of one another. Nevertheless, it is almost universally agreed that two criteria must be met for TiO\textsubscript{2} to perform efficiently as a photocatalyst: the reactants, including electron- and hole-trapping species, must be adsorbed to the surface prior to illumination; and the recombination of photogenerated electrons and holes must be effectively suppressed.

The purpose of the photocatalysis experiments in the present work is threefold: (1) to evaluate independently and clarify the influences of crystalline phase and specific surface area over photocatalytic efficiency, which essentially amounts to evaluating activity on both a per gram and a per surface area basis; (2) to determine whether the combination of anatase-rutile synergy and high surface area (> 100 m\textsuperscript{2} g\textsuperscript{-1}) might improve the photocatalytic performance of mixed-phase TiO\textsubscript{2} powders relative to that of a commercially available anatase-rutile mixture; and (3) to perform the first experiments testing the importance of morphology and dominant crystallographic faces in determining the efficiency of phase-pure nanocrystalline anatase catalysts. (To simplify the assessment of the effects of each of these physical properties, none of the surface modifications described in Section 5.3.4 were employed in the present studies.) The experimental work used to address each of the above three points, along with a
semiquantitative evaluation of photocatalytic reaction kinetics in the presence of different synthetic TiO₂ nanopowders, is presented in the next chapter.

References


Chapter 6

Photodegradation of Congo Red with nanoscale TiO₂: Influence of grain size, surface area, phase composition, and particle morphology on photocatalytic activity

6.1. Introduction

As seen in Chapter 5, the use of nanocrystalline titania for the photocatalytic oxidative destruction of organic molecules represents a promising remediation strategy for wastewater systems. Various studies of TiO₂-mediated photooxidation reactions during the last three decades have revealed that the efficiency (activity) of a nano-TiO₂ photocatalyst depends to a great extent on its physical properties, including grain size, specific surface area, and phase composition. Such properties determine photocatalytic performance by influencing either the adsorptive properties of a catalyst or the extent of charge separation upon photoinduced generation of electron-hole (e⁻/h⁺) pairs. In general, a photocatalyst’s efficiency increases with its adsorptive capacity and its ability to prolong e⁻/h⁺ separation through the transfer or trapping of charges. Efficient charge separation is particularly critical since the photogenerated holes are required for oxidation of adsorbates, usually through the mediation of an adsorbed OH⁻ group that reacts with a hole to form the powerful oxidant OH⁺.¹

Not surprisingly, small grain sizes and high specific surface areas tend to increase the photocatalytic activity of TiO₂ due to the large number of surface sites available for adsorption and subsequent destruction of contaminant molecules, although there are limits to this beneficial effect since the rate of e⁻/h⁺ may be high in extremely small particles.²⁻⁵ Additionally, it is widely believed that the anatase polymorph of TiO₂, with
its comparatively high adsorptive affinity for organics and its superior hole-trapping ability, is a more efficient photocatalyst than the rutile polymorph.\textsuperscript{1, 6-10} However, it has also been shown that a commercially available mixture of the two phases (i.e., Degussa P25) exhibits superior photocatalytic activity to pure anatase and pure rutile.\textsuperscript{11-18} This latter observation of enhanced activity in mixed-phase catalysts results from a synergistic effect involving prolonged separation of photogenerated electrons and holes through interfacial electron transfer from the conduction band of rutile to the trapping states of anatase.\textsuperscript{16}

Despite the vast body of knowledge about the effect of nano-titania’s physical properties on its photocatalytic behavior, a number of ambiguities and unanswered questions remain. First, is anatase usually a better photocatalyst than rutile because of differences related to the crystal structures, or is it because anatase typically has smaller grains and higher specific surface areas than rutile?\textsuperscript{16} Since most investigators report photocatalytic activities on a per gram basis instead of normalizing the activities to unit surface area, it is not always clear whether anatase’s generally higher surface area skews the results in “favor” of that polymorph.

A second question concerns whether the anatase-rutile synergy reported for Degussa P25 TiO\textsubscript{2} (grain size $\sim$ 20 nm) would also be observed in mixed-phase TiO\textsubscript{2} samples with ultrafine (grain size $< 10$ nm) particles. Additionally, if an ultrafine anatase-rutile mixture was to exhibit such a synergistic effect, would the combination of this synergy and the mixture’s high specific surface area result in an improvement of photocatalytic efficiency over that of the coarser Degussa P25 nanoparticles? If so, would
the relative amounts of anatase and rutile in ultrafine samples affect the activity, as has been reported for coarser samples.\textsuperscript{19}

Lastly, to the author's knowledge, the influence of nanocrystal shape and dominant crystallographic surfaces on the photocatalytic activity of a TiO\textsubscript{2} sample has never been investigated. Previous studies have found that ZnO-mediated photocatalysis is more efficient on the (1 0 -1 0) surface than on the (0 0 0 2) surface.\textsuperscript{20,21} If TiO\textsubscript{2} were found to exhibit a similar face-dependent efficiency, it would represent a valuable new way to optimize the photocatalytic performance of nanocrystalline TiO\textsubscript{2} through the tuning of physical properties. In this case, one could design a TiO\textsubscript{2} catalyst to consist of particles whose dominant crystal faces were best suited for photocatalysis. Such a strategy would be especially useful in the production of oriented thin films of nano-TiO\textsubscript{2}.

This chapter describes a series of photocatalysis experiments that were designed to evaluate independently the effects of grain size, specific surface area, and phase composition on the photocatalytic activity of nanocrystalline TiO\textsubscript{2}. Additionally, mixed-phase TiO\textsubscript{2} catalysts with grain sizes of roughly 5 nm were tested to determine whether the combination of high surface area afforded by small particle sizes and the anatase-rutile synergy previously reported for certain mixed-phase samples would improve the photocatalytic activities of these samples relative to Degussa P25. Finally, the effects of particle morphology on photocatalytic performance were tested by evaluating the activities of isotropic and anisotropic anatase nanocrystals with different proportions of (1 0 1) surface sites.

The model reaction used to characterize photocatalytic behavior in this study was the photodecomposition of aqueous Congo Red (MW = 696.67 g mol\textsuperscript{-1}), a recalcitrant
azo dye found in textile wastewater. Congo Red, whose structure is shown in Figure 6.1, has been the subject of several photocatalysis studies involving commercial TiO$_2$. Some of these studies have established that photocatalytic degradation of the dye proceeds according to a pathway in which nitrogen atoms from the azo functionality are liberated as molecular nitrogen rather than as harmful nitrates, indicating that photocatalysis should be a safe means of eliminating Congo Red from the environment.$^{22-26}$ Because Congo Red tends to degrade slowly in photocatalytic reactions, the differences in the activities of various photocatalysts toward the dye were expected to be more apparent than in the case of a pollutant that degrades very rapidly.

To quantify photocatalytic efficiency, both the half-life $t_{1/2}$ (i.e., the amount of time required for 50% dye removal) and the Langmuir-Hinshelwood kinetic model were used. Implicit in the latter analysis were the following assumptions: (1) Congo Red was adsorbed on TiO$_2$ surfaces according to a Langmuir-type isotherm, i.e.,

\[
\theta = \frac{KC}{1 + KC}
\]  

(6.1)

where $K$ is the adsorption constant and $C$ is the concentration of dye; (2) a constant number of adsorption sites were available at equilibrium; (3) only one Congo Red molecule could occupy a single adsorption site; (4) the rate of adsorption exceeded that of any subsequent reaction; and (5) adsorption was completely reversible.$^6$ As will be seen, a simple, unimolecular Langmuir-Hinshelwood kinetic analysis provided a satisfactory description of the photocatalytic reaction at low dye concentrations but failed at high dye concentrations.
**Figure 6.1.** The structure of Congo Red.

6.2. Experimental

6.2.1. Materials

A commercial anatase-rutile mixture (P25) was kindly supplied by the Degussa Corporation. Tetramethylammonium hydroxide ($1.0 \text{ mol L}^{-1}$, aqueous), titanium (IV) isopropoxide, titanium (IV) chloride, Congo Red, and 2-propanol were purchased from Aldrich; titanium (IV) ethoxide was from Fluka; and hydrochloric acid, sodium hydroxide, and sodium chloride were from Fisher Scientific. All chemicals were used “as received” without further purification.
6.2.2. Preparation of nanocrystalline TiO₂ photocatalyst powders

The reactions and conditions used to prepare the various TiO₂ powders used in this study are summarized in Table 6.1. The synthetic routes to anatase dots, anatase rods, and ultrafine rutile and mixed-phase powders are separately described in detail in the following sections.

Table 6.1. Synthetic conditions for nanosized TiO₂ photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthetic method</th>
<th>Precursor</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Passivating agent</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>Aerosol (proprietary)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HT-184</td>
<td>Hydrothermal, no surfactant</td>
<td>Ti(OEt)₄</td>
<td>EtOH</td>
<td>150</td>
<td>None</td>
<td>2</td>
</tr>
<tr>
<td>CA-P</td>
<td>Hydrothermal, low surfactant concentration</td>
<td>Ti(OPr)₄</td>
<td>H₂O</td>
<td>90-100 (reflux), 180-190 (hyd. trt.)</td>
<td>TMAH</td>
<td>6 (reflux), 5 (hyd. trt.)</td>
</tr>
<tr>
<td>CE-P</td>
<td>Hydrothermal, high surfactant concentration</td>
<td>Ti(OPr)₄</td>
<td>H₂O</td>
<td>90-100 (reflux), 180-190 (hyd. trt.)</td>
<td>TMAH</td>
<td>6 (reflux), 5 (hyd. trt.)</td>
</tr>
<tr>
<td>R1</td>
<td>Hydrolytic, acid peptization</td>
<td>TiCl₄</td>
<td>H₂O</td>
<td>85</td>
<td>HCl (pH -1)</td>
<td>2</td>
</tr>
<tr>
<td>R2</td>
<td>Hydrolytic, acid peptization</td>
<td>TiCl₄</td>
<td>H₂O</td>
<td>100</td>
<td>HCl (pH -1)</td>
<td>2</td>
</tr>
<tr>
<td>AR1</td>
<td>Hydrolytic, acid peptization</td>
<td>TiCl₄</td>
<td>H₂O</td>
<td>100</td>
<td>HCl (pH –0.27)</td>
<td>2</td>
</tr>
<tr>
<td>AR2</td>
<td>Hydrolytic, acid peptization</td>
<td>TiCl₄</td>
<td>H₂O</td>
<td>100</td>
<td>HCl (pH 0.25)</td>
<td>2</td>
</tr>
</tbody>
</table>
6.2.2.1. Anatase dots

The surfactant-free hydrothermal synthesis described in Chapter 3 affords a fast, simple, and reliable route to anatase nanocrystals with grain sizes of 10 nm or less and specific surface areas in excess of 150 m$^2$ g$^{-1}$. For the photocatalysis experiments detailed in this chapter, anatase dots were prepared from titanium (IV) ethoxide according to the procedure in Section 3.2.2 using a Ti(OEt)$_4$ concentration of 0.32 mol L$^{-1}$, a water:alkoxide ratio of $r = 20$, and a total reaction time of 2 h. The product was filtered using Whatman Type 2 ashless filter paper, washed twice with H$_2$O, and dried overnight in a 60 °C oven prior to characterization.

6.2.2.2. Anatase rods with tunable aspect ratios

To test the effects of nanoparticle anisotropy on the photocatalytic efficiency of TiO$_2$, rodlike anatase nanocrystals were prepared with two different aspect ratios. These anatase nanorod samples were synthesized using a scaled-up version of the surfactant-based method developed by Chemseddine and Moritz.$^{27}$ Briefly, a dilute solution of tetramethylammonium hydroxide (TMAH) was prepared by adding aqueous TMAH reagent (1.0 mol L$^{-1}$; 2.6 mL for short rods, 13.6 mL for long rods) to 1500 mL H$_2$O in a 2000-mL, three-neck roundbottom flask equipped with a stir bar. The surfactant solution was cooled to 4-5 °C in an ice bath, after which a solution of titanium (IV) isopropanoxide (3.33 mL, 1.14 mmol) in 2-propanol (100 mL) was poured into the flask. The resulting turbid white suspension was stirred at low temperature (~ 8 °C) for 10 min. and then refluxed at 90-100 °C for 6 h. After the first 3 h of refluxing, the TiO$_2$ suspension turned
clear; by the end of the reflux period, however, the colloid had become slightly turbid once again. Coarsening of the TiO₂ nanoparticles to obtain rodlike crystallites was accomplished by hydrothermally treating the refluxed suspension (150-250 mL at a time) for 5 h at 180-190 °C.

If left undisturbed, the hydrothermally treated colloids remained stable at room temperature for several months; in fact, the TMAH surfactant stabilized individual nanocrystals so effectively that even vigorous centrifugation (4200 rpm) over a period of several hours could only remove a very small amount of TiO₂ powder from suspension. To obtain TiO₂ nanorods in powder form, then, it was necessary to crash out the particles by adding solid NaCl to the colloidal suspensions. The resulting white precipitate was collected by centrifugation, washed twice with H₂O, and finally dialyzed against MilliQ H₂O for at least 24 h in order to remove any residual surfactant as well as any remaining Na⁺ or Cl⁻ ions. The washed powder was dried in a 60 °C oven overnight prior to characterization.

The nanorod samples were analyzed by Fourier Transform Infrared (FTIR) spectroscopy to confirm the removal of surfactant from the TiO₂ surfaces by washing and dialysis. This analysis was performed on a Nicolet Avatar 370 apparatus, using 30 scans per spectrum and a resolution setting of 4.0.

6.2.2.3. Ultrafine rutile and mixed-phase catalysts

Two samples of phase-pure rutile (R1 and R2) and two anatase-rutile mixtures (AR1 and AR2) were prepared at grain sizes of 5 nm or less using a modified version of
an acid reflux method reported by Cheng et al. The general procedure was as follows: titanium (IV) chloride (47.0 g, 0.25 mol) was added slowly to MilliQ H₂O (450 mL) in a 500-mL volumetric flask to produce a white suspension. HCl (37.5%, 50 mL) was added to the suspension as a peptizing agent, and after stirring overnight the mixture turned clear.

Then, to prepare each sample, a 100-mL portion of the peptized TiO₂ suspension was adjusted to the desired pH (-1 for rutile samples R1 and R2, -0.25 for AR1, and 0.27 for AR2) by addition of NaOH, after which it was heated to either 85 °C (R1) or 100 °C (R2, AR1, AR2) and refluxed for 2 h. The resulting white powder was crashed out of suspension, centrifuged, washed, dialyzed, and dried in the manner described in Section 6.2.2.2.

6.2.3. TiO₂ sample characterization

All TiO₂ powders were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer- Emmett-Teller (BET) surface area analysis, and differential thermal analysis (DTA) using the procedures and equipment described in Section 3.2.3. However, estimation of average grain sizes from XRD linewidths was only possible in the case of the anatase dots, the rutile samples, and the laboratory-synthesized anatase-rutile mixtures, as individual crystallites in the other samples were larger than 20 nm and therefore too large to cause any substantial line broadening in a powder XRD spectrum. When size estimation from XRD linewidths was not possible, particle sizing was done using TEM images.
6.2.4. Adsorption isotherms

For a Langmuir-Hinshelwood analysis of photocatalytic rate data to be valid, it is necessary for the system under study to have reached adsorption equilibrium prior to ultraviolet irradiation. To determine the time required for the various Congo Red-TiO$_2$ suspensions to reach adsorption equilibrium, an adsorption isotherm was constructed for each suspension as follows: first, 100 mg of the TiO$_2$ powder was dispersed via sonication in 50 mL H$_2$O in a capped 125-mL bottle equipped with a stir bar. The bottle was then wrapped in aluminum foil to shield the contents from light, and 50 mL of a 100 mg L$^{-1}$ (144 µmol L$^{-1}$) aqueous solution of Congo Red was added to the TiO$_2$ suspension, resulting in a total dye concentration of 50 mg L$^{-1}$ (72 µmol L$^{-1}$). The bottle’s contents were stirred in the dark for a total of 27 h, with 4-mL aliquots withdrawn at predetermined times for analysis.

Each aliquot was centrifuged for 4 min. at 14000 rpm to remove the TiO$_2$ powder, after which the aqueous supernatant was carefully transferred into a polystyrene cuvette and its UV-vis spectrum taken. The concentration of Congo Red in the supernatant fluid was calculated from the absorbance at 496 nm; this number was then subtracted from the nominal total dye concentration (i.e., 72 µmol L$^{-1}$) to obtain the amount of dye adsorbed to the surfaces of TiO$_2$ nanoparticles.

Figure 6.2 shows sample adsorption isotherms for Congo Red in the presence of selected TiO$_2$ powders. The suspension containing the commercial anatase-rutile mixture from Degussa required only 1 h of equilibration time, while it took considerably longer (21 – 24 h) for the dye to reach adsorption equilibrium in the presence of the seven laboratory-made samples.
Figure 6.2. Adsorption isotherms for aqueous Congo Red (50 mg L\(^{-1}\), 72 \(\mu\)mol L\(^{-1}\)) in the presence of different nano-TiO\(_2\) photocatalysts. All samples required 21 – 24 h to reach adsorption equilibrium (panel a), with the exception of Degussa P25, which only required 1 – 2 hours (panel b). The equilibrium amounts of adsorbed dye indicate that anatase and mixed-phase catalysts had greater adsorptive affinities than rutile catalysts.

(a)

(b)

- Degussa P25 mixture
- R1 rutile dots
- HT-184 anatase dots
- AR1 mixture
6.2.5. Photodegradation of Congo Red with nanocrystalline TiO₂

6.2.5.1. Photocatalytic reactions

Photocatalytic degradation of Congo Red in the presence of different nanocrystalline TiO₂ samples was carried out as follows: first, 10 mg TiO₂ powder was sonicated in a predetermined volume (7.0 – 9.9 mL) of MilliQ H₂O in a Pyrex scintillation vial equipped with a stir bar and sealed with a rubber septum. The vial was wrapped in aluminum foil and a predetermined volume (0.1 – 3.0 mL) of aqueous Congo Red stock solution (100 mg L⁻¹, 144 μmol L⁻¹) was added to bring the total volume in the vial to 10.0 mL. The total TiO₂ mass concentration was 1.0 g L⁻¹ in all cases; initial Congo Red concentrations ranged from 1.0 to 30 mg L⁻¹ (1.44 to 33.2 μmol L⁻¹) for all samples except CA-P, for which there was only enough TiO₂ to perform experiments for initial concentrations between 1.0 and 10 mg L⁻¹ (1.44 to 14.4 μmol L⁻¹).

Each suspension was stirred in the dark for at least 24 h (or 1 h in the case of the Degussa P25 sample) to ensure adsorption equilibrium was established prior to irradiation. It was assumed that the minimum equilibration times determined from the adsorption isotherms in Figure 6.2 would be adequate for the Congo Red concentrations tested in the photocatalysis experiments, since all of these concentrations were lower than that used to determine the adsorption isotherms. After the pre-adsorption period, the foil was removed from the scintillation vial and a ventilation needle was inserted through the septum to allow any gaseous products (e.g., CO₂) to escape during photodegradation of the dye. After an initial UV-vis spectrum was collected for the dye-TiO₂ suspension (information on spectrum collection and analysis is included in the next section), the vial
Figure 6.3. Photographs of the Luzchem Model 4-V photoreactor. (a) Interior of the reactor. (b) An aqueous Congo Red-TiO₂ suspension under UV-A illumination (maximum emission at λ = 350 nm).
was placed inside a Luzchem Model 4-V photoreactor (Figure 6.3a) equipped with a magnetic stirrer and 14 UV-A lamps with an emission maximum at $\lambda = 350$ nm. The sample was irradiated (Figure 6.3b), with stirring, for a predetermined amount of time, after which the lamps were turned off and a 3-mL aliquot was withdrawn for UV-vis analysis. Once a spectrum was collected, the aliquot was returned to the vial and the sample was irradiated for another interval. The sequence of sample illumination and aliquot analysis was repeated until enough data had been collected to determine the initial degradation rate (see Section 6.3.2 below for details of initial rate estimation).

Additionally, for each powder a photodegradation run with an initial dye concentration of 10 mg L$^{-1}$ was carried out to completion, i.e., until the Congo Red concentration was zero. The times required for 50% dye removal in this latter set of experiments were denoted as $t_{1/2}$. The $t_{1/2}$ values were expressed both on a mass basis (min g) and on a unit surface area basis (min m$^2$), so as to evaluate the influence of both surface area and properties inherent in the crystal structure on photocatalytic activity.

6.2.5.2. UV-visible characterization

UV-visible spectra for dye-TiO$_2$ suspensions were collected on a Cary 5000 spectrophotometer using a 1.0 g L$^{-1}$ aqueous suspension of the relevant TiO$_2$ sample as the reference. The reason for leaving the solid TiO$_2$ in the aliquots instead of removing it by centrifugation or filtration was that any dye adsorbed to the TiO$_2$ surfaces would have been removed along with the solid, making it impossible to determine the total concentration of dye as a function of time. Although many investigators typically remove the solid catalyst prior to characterizing aliquots in photocatalysis experiments, in doing
so they are effectively analyzing only the reactant present in solution, neglecting whatever reactant is present on the catalyst surface at the time the aliquots are withdrawn. Because of the importance of surface processes in photocatalysis, it was decided that the total UV-vis absorbance, i.e., the absorbance due to both surface adsorbed dye and free dye in solution, would be used to monitor the kinetics of Congo Red photodegradation.

It was important to consider two issues during this analysis. First, because TiO$_2$ absorbs light with $\lambda < 400$ nm, useful spectral information could only be obtained at wavelengths above 400 nm; therefore the UV-vis spectra for these experiments were collected over the wavelength range 400 – 800 nm. The inability to analyze the aliquots at $\lambda < 400$ nm meant that only one of the two major absorption features in the UV-vis spectrum of Congo Red – namely, the peak at $\sim 496$ nm – could be monitored as a function of irradiation time, since the other feature occurs around 345 nm.

Additionally, the scattering of light by TiO$_2$ had to be taken into account during analysis, which in practical terms meant that the contribution of TiO$_2$-scattered light to the absorbance had to be subtracted out from each individual UV-vis spectrum; fortunately, within a given photodegradation experiment these contributions remained essentially the same from spectrum to spectrum, varying only in their absolute positions on the y-axis; thus they could be baselined with reasonable reliability using the procedure described in the next section.
**Figure 6.4.** UV-visible spectrum of an aqueous Congo Red-TiO$_2$ suspension (a) before and (b) after baselining. The dotted line in (a) represents the baseline.
6.3. Data analysis

6.3.1. Analysis of UV-visible spectra

Before using UV-visible absorbance values to calculate the Congo Red concentration in each aliquot from the photocatalysis runs, it was necessary to apply a baselining routine to most of the raw UV-vis spectra. Despite the use of a TiO$_2$ suspension as a reference standard, the solid nanoparticles present in the dye-TiO$_2$ samples scattered light such that the automatic baseline correction featured in the Cary instrument’s software was insufficient to properly level and zero the experimental UV-vis spectra; for this reason, it was necessary to manually baseline individual spectra. The manual baselining procedure for each spectrum was as follows: first, since the UV-vis profile of Congo Red is normally flat over the range 700 – 800 nm, a straight line was fitted to the experimental spectrum in this range. The equation corresponding to this line had the form $A = m\lambda + b$, with $A$ representing the absorbance, $\lambda$ the wavelength in nm, and $m$ and $b$ the slope and intercept of the line respectively. This linear function was then subtracted from the raw spectrum to obtain a properly baselined spectrum, as illustrated in Figure 6.4. This procedure proved adequate for all samples except AR2, for which the baseline was more complicated; in this case the efficiency of the catalyst was characterized by noting the time at which the absorbance feature at 496 nm disappeared completely and then estimating the half-life based on comparison with the results for AR1, whose behavior turned out to be almost identical to that of AR2 on a per gram basis.
Once the UV-vis spectra were corrected, the concentration of Congo Red in each aliquot was calculated from the absorbance at 496 nm, the value of $\lambda$ where the dye-TiO$_2$ suspensions exhibited an absorbance maximum. Absorbance values were converted to concentrations by assuming the $A_{496}$ value at $t = 0$ corresponded exactly to the nominal initial dye concentration and then using a simple Beer's Law proportionality, i.e.,

$$\frac{A_{496}}{[CR]_0} = \frac{A_{496}}{[CR]_t}$$  \[(6.2)\]

to determine the amount of dye $[CR]_t$ at any subsequent time $t$. (UV-vis analysis of a series of calibration standards revealed that Beer's Law was valid – i.e., absorbance was directly proportional to concentration – for dye concentrations up to 40 mg L$^{-1}$ for all dye-TiO$_2$ suspensions. However, because of the substantial day-to-day variability of absorbance magnitudes for such suspensions, it was not possible to calculate Congo Red concentrations using a single calibration curve for experiments performed on different days. This is why concentrations were instead determined using the assumption of nominal initial concentrations as described above.)
Figure 6.5. Procedure for estimating the initial rate ($r_0$) of Congo Red degradation from a plot of concentration ($C$) versus time ($t$). The slope of the nearly linear region of the degradation profile at early times was taken to be $r_0$. 
6.3.2. Initial rate determination

Initial degradation rates were estimated for different initial dye concentrations in order to quantify photocatalytic activity by Langmuir-Hinshelwood analysis. In each plot of Congo Red concentration as a function of time, there was an interval \(0 \leq t \leq t_i\) during which the concentration decreased nearly linearly. This interval was very short for Degussa P25, HT-184, AR1, and AR2 (\(t_i = 0.5 - 1\) min.) and somewhat longer for CA-P, CE-P, R1, and R2 (\(t_i = 5 - 10\) min.). Each initial degradation rate \(r_0 = \frac{[\text{d}C]}{[\text{d}t]}|_0\) was estimated by fitting the concentration vs. time data between \(t = 0\) and \(t = t_i\) with a straight line, the slope of which was taken to be \(-r_0\) (see Figure 6.5).

6.3.3. Langmuir-Hinshelwood kinetic analysis

Surface catalyzed reactions can often be adequately described by a unimolecular Langmuir-Hinshelwood mechanism, in which an adsorbed reactant with fractional surface coverage \(\theta\) is consumed at an initial rate given by

\[
\left. \frac{\text{d}C}{\text{d}t} \right|_0 = r_0 = k\theta = \frac{kC_0}{1 + KC_0}
\]  

(6.3)

where \(k\) is a rate constant that increases with increasing photocatalytic activity, \(K\) is the adsorption equilibrium constant, and \(C_0\) is the total initial reactant concentration. A sample plot of \(r_0\) versus \(C_0\) for such a kinetic regime is shown in Figure 6.6a. Inversion of the above rate equation yields
Figure 6.6. Schematic illustration of Langmuir-Hinshelwood analysis. For a reaction that follows unimolecular Langmuir-Hinshelwood kinetics, (a) a plot of the initial rate $r_0$ against the initial concentration $C_0$ should exhibit a positive slope at low $C_0$ followed by a plateau at high $C_0$, while (b) a plot of $r_0^{-1}$ against $C_0^{-1}$ should yield a straight line with slope $(kK)^{-1}$ and intercept $k^{-1}$, where $k$ is the rate constant and $K$ is the adsorption equilibrium constant.
\[
\frac{1}{r_0} = \frac{1}{kK} \frac{1}{C_0} + \frac{1}{k}
\] (6.4)

Thus if Langmuir-Hinshelwood kinetics are applicable, a plot of \(r_0^{-1}\) against \(C_0^{-1}\) should be a straight line with slope \((kK)^{-1}\) and intercept \(k^{-1}\) (see Figure 6.6b).\(^6\) Such an analysis allows one to quantify the photocatalytic activity of a TiO\(_2\) powder through the rate constant \(k\), with larger \(k\) values corresponding to higher photocatalytic efficiency.

It is important to note that implicit in the unimolecular version of Langmuir-Hinshelwood analysis is the assumption – or, more accurately, the approximation – that the concentration of dye alone determines the degradation rate. Such an approximation has been made and found to be reasonable in previous kinetic studies of photocatalysis, even though from a mechanistic standpoint the photooxidative degradation of a dye (or other species) more likely involves a bimolecular reaction between the dye and a surface adsorbed OH\(^*\) radical.\(^{29,30}\) Properly speaking, then, the rate of disappearance of the dye should be calculated as:

\[
-\frac{dC}{dt}\bigg|_{t_0} = \frac{kK_{dye}C_{0,dye}}{1 + K_{dye}C_{0,dye} + K_{OH^*}C_{0,OH^*}}
\] (6.5)

This is assuming, of course, that OH\(^*\) does not have to compete with some other oxidant, e.g., photogenerated holes that have been trapped but have not accessed surface hydroxyls to form OH\(^*\). Such an assumption has been validated in numerous studies that
have pointed to OH$^*$ as the primary oxidant in most photocatalytic reactions involving TiO$_2$.\textsuperscript{31,43}

The reason one can usually afford to neglect the participation of a second, competitively adsorbed species – in this case, OH$^*$ – when evaluating the kinetics of a photocatalytic reaction is that the concentration of OH$^*$ on the catalyst surface is usually much larger than that of the species undergoing photodecomposition, so that $C_{0,\text{OH}*}$ can be treated as essentially constant and the rate depends primarily on variations in $C_{0,\text{dye}}$. In such cases equations 6.3 and 6.4 may be used. However, even under these conditions one must be aware that the constants $k$ and $K$ determined from a unimolecular Langmuir-Hinshelwood analysis are actually the apparent rate constant and apparent adsorption constant, i.e., the effects of competitive adsorption of OH$^*$ are embedded in the experimental values obtained for $k$ and $K$. The apparent adsorption equilibrium constant is in this case $K = K_{\text{dye}} / (1 + K_{\text{OH}*}C_{0,\text{OH}*})$.\textsuperscript{6,44}

Because of the extreme difficulty in measuring the concentration of OH$^*$ radicals on the surface of TiO$_2$ during photocatalysis, the unimolecular-reaction approximation was made for the purposes of Langmuir-Hinshelwood analysis in the present work, i.e., equations 6.3 and 6.4 were used to determine $k$ and $K$. Given this approximation, plots of $r_0^{-1}$ vs. $C_0^{-1}$ (where $r_0$ and $C_0$ are now abbreviations for $r_{0,\text{dye}}$ and $C_{0,\text{dye}}$ respectively) were constructed for each TiO$_2$ photocatalyst and evaluated for linearity. These plots tended to be linear over a limited range corresponding to low initial dye concentrations, so the data in this range were fitted with a line that was then extrapolated to $C_0^{-1} = 0$ to determine the slope (i.e., $(kK)^{-1}$) and intercept (i.e., $k^{-1}$).
Table 6.2. Physical characteristics of nanosized TiO\textsubscript{2} photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle shape</th>
<th>Phase(s)</th>
<th>$D_{\text{avg}}$ (nm)</th>
<th>SSA (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Amorphous content</th>
<th>Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>Spherical</td>
<td>A/R (80:20)</td>
<td>~21</td>
<td>~50</td>
<td>None</td>
<td>Yes</td>
</tr>
<tr>
<td>HT-184</td>
<td>Spherical</td>
<td>A</td>
<td>10.1</td>
<td>153</td>
<td>None</td>
<td>Yes</td>
</tr>
<tr>
<td>CA-P</td>
<td>Short rod</td>
<td>A</td>
<td>~50 (long axis)</td>
<td>94.5</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>CE-P</td>
<td>Long rod</td>
<td>A</td>
<td>~150 (long axis)</td>
<td>28.0</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>R1</td>
<td>Spherical</td>
<td>R</td>
<td>3.17</td>
<td>112</td>
<td>None</td>
<td>Yes</td>
</tr>
<tr>
<td>R2</td>
<td>Spherical</td>
<td>R</td>
<td>5.41</td>
<td>110</td>
<td>None</td>
<td>Yes</td>
</tr>
<tr>
<td>AR1</td>
<td>Pillbox</td>
<td>A/R (40:60)</td>
<td>5.21 (A), 5.41 (R)</td>
<td>232</td>
<td>None</td>
<td>Yes</td>
</tr>
<tr>
<td>AR2</td>
<td>Pillbox</td>
<td>A/R (70:30)</td>
<td>5.17 (A), 5.01 (R)</td>
<td>123</td>
<td>None</td>
<td>Yes</td>
</tr>
</tbody>
</table>

6.4. Results and discussion

6.4.1. Characterization of photocatalyst powders

Results from XRD, TEM, and BET analysis are reported in Table 6.2. The XRD patterns for the various TiO\textsubscript{2} powders, shown in Figure 6.7, indicate that Degussa P25 consists of approximately 80\% anatase and 20\% rutile; HT-184, CA-P, and CE-P are pure anatase; R1 and R2 are pure rutile; and AR1 and AR2 consist of the anatase and rutile phases, with anatase:rutile mass ratios of approximately 40:60 and 70:30.
Figure 6.7. X-ray diffraction (XRD) patterns for nanocrystalline TiO$_2$ photocatalyst powders. Samples HT-184, CA-P, and CE-P were phase-pure anatase; samples R1 and R2 were phase-pure rutile; and samples P25, AR1, and AR2 were mixtures of anatase and rutile. AR1 and AR2 also contained trace amounts of the brookite phase.

respectively (phase compositions of the anatase-rutile mixtures were estimated by taking the ratio of the integrated intensities of the anatase (1 0 1) and rutile (1 1 0) peaks and comparing it to the corresponding ratio in standard anatase-rutile mixtures of known mass compositions). Small amounts of brookite were also detected in the AR1 and AR2 samples. In the case of HT-184, R1, R2, AR1, and AR2, line broadening due to finite size effects was large compared to instrumental broadening and it was possible to estimate
Figure 6.8. Transmission electron micrographs (TEMs) of nano-TiO$_2$ samples: (a) HT-184 anatase dots, (b) CA-P anatase short rods, (c) CE-P anatase long rods, (d) R1 rutile dots, (e) R2 rutile dots, (f) AR1 mixed-phase dots, and (g) AR2 mixed-phase dots. Samples prepared without a surfactant (HT-184, R1, R2, AR1, and AR2) exhibited moderate to severe aggregation, with R1 and R2 in particular displaying a tendency to form large aggregated structures. In contrast, rodlike anatase samples (CA-P) and (CE-P) prepared in the presence of tetramethylammonium hydroxide (TMAH) exhibited little or no aggregation and were dominated by anatase (1 0 1) surfaces.
Figure 6.8 (continued).
average grain sizes from the anatase (1 0 1) linewidth and/or the rutile (1 1 0) linewidth. The (1 1 1) reflection of an internal silicon powder standard was used to correct for instrumental broadening (see Section 3.2.3 for more details).

Transmission electron micrographs (TEMs) for each laboratory-made sample are shown in Figure 6.8. It is immediately apparent from these images that the particles prepared in the presence of TMAH (CA-P and CE-P) were significantly less aggregated than those prepared without any surfactant, even despite the presence of HCl as a peptizing agent during the synthesis of the rutile and mixed-phase samples; in fact, aggregation among the rutile nanocrystals was so prevalent that many of the primary particles in samples R1 and R2 appear to have actually self-assembled into large, striated structures. Furthermore, in contrast to the spherical (HT-184, R1, and R2) or pillbox-like (AR1 and AR2) morphologies exhibited by the TiO$_2$ samples prepared without TMAH, the CA-P and CE-P nanocrystals exhibited striking rodlike morphologies, with high surfactant concentrations (CE-P) yielding larger aspect ratios and larger particles than low surfactant concentrations (CA-P).

According to Chemseddine and Moritz, the (1 0 1) surfaces are dominant in samples prepared by their method. They attributed this anisotropy to the selective binding of the tetramethylammonium cation (N(CH$_3$)$_4^+$) to the (1 0 1) surfaces, which inhibits growth in the [1 0 1] direction and encourages growth in perpendicular directions.$^{27}$ The higher the surfactant concentration, the more pronounced this anisotropic effect is.

BET surface areas ranged from 28 to 232 m$^2$ g$^{-1}$ and were found to increase in the order CE-P < P25 < CA-P < R1 ≡ R2 < AR2 < HT-184 < AR1, corresponding in most cases to a decrease in average crystallite size. Sample AR1 had an unexpectedly high
**Figure 6.9.** A sample differential thermal analysis (DTA) profile of a nano-TiO$_2$ photocatalyst. The endothermic peak near 100 °C corresponds to evaporation of adsorbed water, while the absence of a sharp exothermic peak between 350 and 450 °C indicates the complete crystallinity (i.e., zero amorphous content) of the material. All the samples investigated in the present study exhibited DTA profiles similar to the one shown here.

![DTA profile](image)

**Figure 6.10.** Fourier transform infrared (FTIR) spectra of (a) tetramethylammonium hydroxide (TMAH) and (b) CE-P anatase after washing and dialysis. The absence of characteristic TMAH resonances in spectrum (b) confirms that washing and dialysis effectively removed the surfactant from the anatase particle surfaces. Sample CA-P exhibited a spectrum (not shown) similar to that of CE-P.

![FTIR spectra](image)
specific surface area, which may be attributable to high porosity. However, since the R1, R2, and AR2 samples were prepared using the same general method as was used for AR1, it is unclear why AR1 would possess such high porosity as to render its surface area nearly twice as large as in those other three powders. This question currently remains unresolved.

Differential thermal analysis (DTA) was used to evaluate the amorphous content of the TiO₂ samples. None of the DTA profiles exhibited an exothermic peak between 350 and 450 °C, thus confirming the complete crystallinity of the powders (Figure 6.9).

Figure 6.10 shows the infrared spectrum for sample CE-P after washing and dialysis, along with the spectrum for aqueous TMAH; the absence of any characteristic TMAH peaks in the spectrum of either of these anisotropic TiO₂ samples indicates that the surfactant was successfully removed from the nanocrystal surfaces by washing and dialyzing against H₂O. This result was also observed for sample CA-P (spectrum not shown).

6.4.2. Photocatalytic decomposition of Congo Red: comparison of TiO₂ photocatalysts

Figure 6.11 shows the degradation profile for a 10 mg L⁻¹ (1.435 μmol L⁻¹) aqueous Congo Red solution in the presence of various TiO₂ powders (mass concentration 1 g L⁻¹). The dye decomposition curves indicate that the HT-184 and commercial P25 catalysts were comparably efficient (t₁/₂ = 1.5 – 3.5 min g) on a mass basis, while the mixed-phase powder AR1 took slightly longer (t₁/₂ ≡ 5 min g) to degrade the dye. Although quantitative determination of dye concentration was not possible for
Figure 6.11. Degradation profiles for aqueous Congo Red (10 mg L$^{-1}$, 14 mmol L$^{-1}$) in the presence of various nano-TiO$_2$ catalysts (1 g L$^{-1}$). Based on this plot, the per gram efficiencies of the TiO$_2$ powders increased in the order R1 < CE-P < CA-P < AR1 < P25 < HT-184.
Figure 6.12. Examples of Langmuir-Hinshelwood analysis of Congo Red photodegradation data: (a) \( r_0 \) versus \( C_0 \) on (i) a per gram basis and (ii) a unit surface area basis; (b) reciprocal plots on (i) a per gram basis and (ii) a unit surface area basis; and (c) fitting the linear portions of the reciprocal plots to determine the parameters \( k \) and \( K \).

Figure 6.12a.
Figure 6.12b.
the AR2 samples because of the complexity of the UV-vis spectral baselines, the absorbance feature at 496 nm disappeared in 60 min for both AR1 and AR2. Therefore the latter’s $t_{1/2}$ value was assumed to be comparable to that of AR1 on a mass basis.

In contrast, the photocatalytic reaction was considerably slower ($t_{1/2} = 15 - 30$ min g) in the presence of the CA-P and CE-P anatase nanorod samples and prohibitively slow ($t_{1/2} \approx 120$ min g) in the presence of the nano-rutile sample R1 (the curve for R2 is not shown in Figure 6.11, but the sample’s efficiency was comparable to that of R1). The $t_{1/2}$ values obtained for each sample are listed in Table 6.3.
Langmuir-Hinshelwood analysis of the initial rate data for each powder provided an additional quantitative comparison of the TiO$_2$ samples’ photocatalytic efficiency. Figures 6.12a and 6.12b show, respectively, $r_0$ versus $C_0$ and $r_0^{-1}$ versus $C_0^{-1}$ plots for two different powders over the entire range of initial dye concentrations tested. The concentration ranges over which the reciprocal plots (examples in Figure 6.12b) were linear in accordance with Langmuir-Hinshelwood predictions, i.e., the ranges defined by $C_0 < x \ \mu$mol L$^{-1}$, are specified in Table 6.3; in general, the value of $x$ was larger for the

Table 6.3. Kinetic parameters for Congo Red photodegradation by various TiO$_2$ powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$t_{1/2}$ (min g)</th>
<th>Specific $t_{1/2}$ (min m$^2$) / $10^2$</th>
<th>Range of L-H applicability ($C_0 &lt; x \ \mu$mol L$^{-1}$)</th>
<th>$k$ (\mu mol g$^{-1}$ min$^{-1}$)</th>
<th>Specific $k$ (\mu mol m$^{-2}$ min$^{-1}$) / $10^{-2}$</th>
<th>$K$ (\mu mol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25 mixture</td>
<td>3.5</td>
<td>1.75</td>
<td>30</td>
<td>4.08</td>
<td>8.15</td>
<td>0.235</td>
</tr>
<tr>
<td>HT-184 anatase dots</td>
<td>1.5</td>
<td>2.30</td>
<td>At least 40</td>
<td>5.11</td>
<td>3.34</td>
<td>0.206</td>
</tr>
<tr>
<td>CA-P anatase short rods</td>
<td>15</td>
<td>14.2</td>
<td>15</td>
<td>1.80</td>
<td>1.90</td>
<td>0.0677</td>
</tr>
<tr>
<td>CE-P anatase long rods</td>
<td>30</td>
<td>8.40</td>
<td>20</td>
<td>0.468</td>
<td>1.67</td>
<td>0.330</td>
</tr>
<tr>
<td>R1 rutile dots</td>
<td>120</td>
<td>134</td>
<td>$\sim$ 8</td>
<td>0.319</td>
<td>0.285</td>
<td>0.584</td>
</tr>
<tr>
<td>R2 rutile dots</td>
<td>--</td>
<td>--</td>
<td>$\sim$ 5</td>
<td>1.60</td>
<td>1.46</td>
<td>0.0266</td>
</tr>
<tr>
<td>AR1 mixture</td>
<td>5</td>
<td>11.6</td>
<td>At least 40</td>
<td>3.57</td>
<td>1.54</td>
<td>0.199</td>
</tr>
<tr>
<td>AR2 mixture</td>
<td>$\sim$ 5</td>
<td>6.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
more efficient photocatalysts, e.g., HT-184 and P25, presumably because the rate of \( \text{OH}^* \) generation in those TiO\(_2\) samples was fast enough to justify the unimolecular Langmuir-Hinshelwood model's assumption of a large, essentially constant concentration of \( \text{OH}^* \) relative to the dye concentration. In contrast, inefficient catalysts such as R1 and R2 would have generated \( \text{OH}^* \) very slowly, so that the \( \text{OH}^* \) concentration would only be large relative to the dye concentration when \( C_0 \) was extremely small; hence the observed deviations from Langmuir-Hinshelwood behavior for \( C_0 > 10 \ \mu\text{mol} \ \text{L}^{-1} \) or so in such cases.

Although a bimolecular Langmuir-Hinshelwood analysis would be more appropriate than the unimolecular analysis at high \( C_0 \), currently there is no good way to quantify the \( \text{OH}^* \) concentration on the TiO\(_2\) surfaces; thus the bimolecular kinetics could not be applied in the present study. However, it might be possible to correctly predict where the deviations from unimolecular Langmuir-Hinshelwood behavior would occur by constructing computer models that could accept both \( \text{OH} \) and dye concentrations as input parameters. Such simulations have not yet been run but should be relatively easy to design and implement.

Meanwhile, for the present work, Langmuir-Hinshelwood analysis was limited to application of the unimolecular kinetics to the linear regions of the \( r_0^{-1} \) versus \( C_0^{-1} \) plots, i.e., the regions where \( C_0 < x \ \mu\text{mol} \ \text{L}^{-1} \) (examples in Figure 6.12c). Linear fits in these regions yielded values of the rate constant \( k \) and the adsorption equilibrium constant \( K \), which are listed in Table 6.3. For the most part, the order of photocatalytic efficiencies quantified in the form of Langmuir-Hinshelwood rate constants was in agreement with the order of efficiencies quantified as \( t_{1/2} \) values. In cases where \( k \) values contradicted the
t_{1/2} results, the $t_{1/2}$ value was assumed to be the more valid measure of photocatalytic activity since determination of $t_{1/2}$ required fewer calculations and approximations than the determination of $k$.

In the following sections the contributions of various characteristics to the observed photocatalytic activities of the nano-TiO$_2$ samples are individually discussed, with a particular emphasis on the possible factors influencing the degree of anatase-rutile synergy and on the consequences of particle anisotropy from a crystallographic point of view.

6.4.2.1. Effects of grain size and surface area

The kinetic data in Figures 6.11 and 6.12 and Table 6.3 indicate that grain size and surface area are among the most important factors influencing the photocatalytic activity of the samples. Among the pure anatase samples – HT-184, CA-P, and CE-P – the $t_{1/2}$ values decreased and the $k$ values (per gram) increased with decreasing grain size and increasing surface area. Additionally, the small crystallite size (10.1 nm) and high surface area (153 m$^2$ g$^{-1}$) of HT-184 anatase rendered the sample more active than Degussa P25, whose crystallite sizes and surface area were intermediate (21 nm, 50 m$^2$ g$^{-1}$).

Currently there are not enough data to determine exactly how, if at all, the grain size and surface area affected the photocatalytic efficiencies of the mixed-phase samples; this issue is explored in more detail in the following section, as part of the discussion of anatase-rutile synergy, but at this time no firm conclusions can be drawn. Likewise, because the two rutile samples R1 and R2 had nearly identical surface areas and similar
grain sizes and aggregation patterns, the effect of total available surface area on the activity of phase-pure rutile could not be determined. However, as will be seen in the next section, other characteristics inherent in the rutile phase were probably more important than surface area in determining rutile’s activity towards Congo Red.

6.4.2.2. Effects of phase composition

6.4.2.2.1. Phase-pure samples: anatase versus rutile

The phase-pure anatase samples exhibited widely varying activities that appeared to depend not only on grain size and surface area but also on the relative dominance of the (1 0 1) plane; the latter factor will be addressed in Section 6.4.2.3. With respect to phase composition, however, it can be concluded from the current \( t_{1/2} \) data that anatase is invariably a better photocatalyst than rutile, even when the results are normalized to unit surface area. The specific \( t_{1/2} \) values for the anatase samples were found to be 1 – 2 orders of magnitude smaller than that of the R1 rutile dots, indicating that the surface of anatase is better suited to photocatalysis than the surface of rutile. Thus, anatase’s generally superior photocatalytic activity is not merely a result of the typically larger surface areas found in anatase, but rather a result of the fundamental differences between anatase and rutile. Specifically, the poor performance of the two rutile photocatalysts, R1 and R2, suggests that even a high surface area (~ 110 m\(^2\) g\(^{-1}\) for both powders) cannot compensate for the inefficient hole trapping and low adsorptive affinity that typically limit rutile’s efficiency as a photocatalyst.

It is, however, also possible that Cl\(^-\) ions present during the nano-rutile synthesis were adsorbed to the particle surfaces and interfered with the photocatalytic reactions. It
has been previously noted that for certain reactions the presence of Cl\(^-\) tends to reduce the photocatalytic efficiency.\(^{45}\) While the possibility of such Cl\(^-\) "poisoning" cannot be completely ruled out without performing elemental analysis on the TiO\(_2\) powders (this analysis is pending), in the present work it was assumed that the extensive dialysis of the samples against H\(_2\)O effectively removed Cl\(^-\) ions from the photocatalyst powders, thus preventing Cl\(^-\) interference with dye degradation. This assumption was indirectly validated by an experiment in which a portion of HT-184 powder was treated with aqueous NaCl, dialyzed under the same conditions as the rutile and mixed-phase samples, tested in the photocatalytic degradation of a 10 mg L\(^{-1}\) solution of Congo Red, and directly compared to HT-184 that had not been exposed to any Cl\(^-\). The treated and untreated HT-184 samples took exactly the same amount of time to completely decolorize 10 mg L\(^{-1}\) dye solutions, suggesting that Cl\(^-\) was not responsible for the low activities observed in the R1 and R2 samples.

The adsorption isotherms in Figure 6.2 illustrate the low adsorptive affinity of rutile for organics, thus supporting the interpretation that limited adsorption of Congo Red contributed to the low activities of R1 and R2. Additionally, the low value of the apparent adsorption constant K estimated from Langmuir-Hinshelwood analysis for R2 (K = 0.0266) confirms the small degree of adsorption in that sample. However, the K value determined by similar analysis of R1's initial rate data was unreasonably high (K = 0.548) in light of the low adsorptivity indicated for R1 in Figure 6.2, a discrepancy that suggests Langmuir-Hinshelwood analysis is not always a reliable way to determine the reaction parameters k and K.
6.4.2.2.2. Assessment of anatase-rutile synergy in mixed-phase samples

As mentioned previously, on a per gram basis the photocatalytic efficiencies of HT-184 and P25 were comparable, both in terms of their \( t_{1/2} \) values and according to the values of their Langmuir-Hinshelwood rate constants. However, when \( t_{1/2} \) values and \( k \) values were normalized to unit surface area, it was found that P25, an anatase-rutile mixture with intermediate surface area (50 m\(^2\) g\(^{-1}\)), was actually more efficient than HT-184, a pure anatase powder with ultrahigh surface area (153 m\(^2\) g\(^{-1}\)), by nearly a factor of 3. This observation confirms that anatase-rutile synergy plays a significant role in enhancing the photocatalytic activity of P25.

Interestingly, this synergistic effect was not as apparent in the ultrafine anatase-rutile mixture AR1, which despite its extremely high surface area (232 m\(^2\) g\(^{-1}\)) exhibited only an intermediate \( t_{1/2} \) value on a mass basis and a specific \( t_{1/2} \) value comparable to those of the anatase nanorods and the rutile dots. The values of the per gram and specific Langmuir-Hinshelwood rate constants corroborate this observation. On the other hand, sample AR2, which had a surface area of 123 m\(^2\) g\(^{-1}\), took approximately as long as AR1 to completely decolorize a 10 mg L\(^{-1}\) solution of Congo Red, indicating that its efficiency on a per gram basis was about the same as that of AR1. Upon normalization to surface area, then, the specific \( t_{1/2} \) and \( k \) values of AR2 could probably be estimated at \(~6.15\) min m\(^2\) and \(~3\) µmol m\(^{-2}\) min\(^{-1}\) respectively, making AR2’s specific activity either equal to or less than that of HT-184 anatase. Because the surface areas of AR2 and HT-184 were also comparable, it does not appear that anatase-rutile synergy gave AR2 an advantage over phase-pure anatase.
There are three possible explanations for the absence or near-absence of synergistic effects in the laboratory-made anatase-rutile mixtures. First, as has been noted in previous studies on the activities of mixed-phase TiO₂, the photocatalytic efficiency of such mixtures depends in part on the relative amounts of anatase and rutile. Bacsza and Kiwi\textsuperscript{12} reported, for example, that among hydrothermally prepared anatase-rutile powders the highest activity for \( p \)-coumaric acid degradation was observed for an anatase-rutile ratio of 70:30. Ding et al.\textsuperscript{19} noted that photocatalytic activity tended to increase with anatase content among anatase-rutile samples whose phase composition was adjusted via calcination, but it was unclear from their data whether it was the introduction of rutile at high calcination temperatures or the elimination of surface hydroxyls at those same temperatures that was responsible for the correlation between activity and phase composition. In any case, it is possible that in the present study, sample AR1 exhibited low photocatalytic activity because its anatase-rutile ratio (40:60) was not optimal. However, such an explanation cannot be applied in the case of AR2, for which the specific activity was about the same as that of pure nano-anatase even though AR2's anatase-rutile ratio (70:30) was very close to that of P25 (80:20) and equal to the optimal value reported by Bacsza and Kiwi (70:30).

A second possible reason for the lack of enhancement in the photocatalytic activities of AR1 and AR2 is that the grain sizes in these samples were not optimal for anatase-rutile synergy. Although smaller crystallites can improve a photocatalyst’s activity by increasing the available surface area for adsorption, this beneficial effect might be offset at very small grain sizes (D < 10 nm) by an increase in band gap energy and e⁻/h⁺ recombination probability.\textsuperscript{3,5} There exists some controversy regarding whether
the latter two size-related effects are important in determining photocatalytic behavior; but, as seen in Section 5.3.1, there have been numerous reports of an optimal crystallite size for which a TiO$_2$ powder's photocatalytic efficiency is maximized. $^{3-5}$ This ideal size has varied from report to report, suggesting that its value depends on either the specific reaction or the photocatalyst preparation method; thus it is difficult to say for certain whether the grain sizes in samples AR1 and AR2 are close to or far from the optimal dimensions for Congo Red decomposition under the conditions studied in the present work.

Finally, the limited or nonexistent synergy in AR1 and AR2 is related to the nature of the anatase-rutile interface in these samples. As mentioned in Section 5.3.2.2, contact between the anatase and rutile phases in mixed-phase TiO$_2$ is essential for any appreciable increase in photocatalytic activity, since such contact allows electrons to be transferred from rutile to anatase thus increasing the charge separation necessary for efficient photocatalytic reaction at the particle surfaces. $^{16}$ This criterion is met in P25, $^{15, 46}$ which accounts partially for its high activity, but in the ultrafine mixed-phase samples the anatase-rutile interfacial contact was not as good.

6.4.2.3. Effects of morphology on the activity of anatase

An important observation in this work was that on a unit surface area basis, phase-pure anatase rods performed poorly as photocatalysts. Because FTIR spectroscopy (Figure 6.10) confirmed the removal of surfactant from the rodlike samples prior to the photocatalytic experiments, surfactant poisoning could be ruled out as a reason for the low activities of the CA-P and CE-P powders. The surface areas of the samples account
at least in part for the differences in their per gram activities, but the fact that the specific activity of the HT-184 dots was larger than that of either the CA-P short rods or the CE-P long rods suggests an additional property affected the efficiencies of the three samples. In particular, the CA-P and CE-P samples consisted of rods in which the anatase (1 0 1) surfaces were dominant, indicating that a large number of (1 0 1) sites was detrimental to the photocatalytic efficiency. However, it was not entirely clear whether the CE-P long rods, with the largest number of (1 0 1) surface sites, were more or less photocatalytically active than the CA-P rods, with an intermediate number of (1 0 1) surface sites. Specific $t_{1/2}$ values suggest that the long rods were slightly more efficient than the short rods, while specific $k$ values suggest that the reverse was true. In either case, though, the predominance of (1 0 1) surfaces in both rodlike samples gave them a clear disadvantage in comparison with the highly efficient HT-184 dots, which had a smaller proportion of (1 0 1) sites.

A rationale for the observed deleterious effect of (1 0 1) surfaces on photocatalytic performance can be found upon examination of the modes of water adsorption to different anatase surfaces. As discussed in Section 5.3.3, first-principles calculations have indicated that water molecules tend to adsorb dissociatively (i.e., as $H^+$ and $OH^-$) to anatase (0 0 1) faces but non-dissociatively (i.e., as $H_2O$) to anatase (1 0 1) faces.\textsuperscript{47, 48} In the latter case, the number of hydroxyl groups present on the surface is expected to be small, which in turn would mean that the number of $OH^+$ radicals generated upon irradiation would also be small. Because $OH^+$ radicals are thought to be the primary oxidizing species in photocatalytic oxidation reactions, it follows that anatase
(1 0 1) faces are probably less active in such reactions than (0 0 1) faces or other surfaces to which water adsorbs in a primarily dissociative fashion.

6.5. Summary and future work

The photoinduced decomposition of Congo Red in aqueous solution has been used to evaluate the photocatalytic activity of nanocrystalline TiO₂ as a function of several physical properties, including grain size, surface area, phase composition, and morphology. Photocatalytic activity was quantified using both half-life measurements (t₁/₂) and Langmuir-Hinshelwood kinetics.

The validity of unimolecular Langmuir-Hinshelwood kinetics for the photocatalytic destruction of Congo Red was limited to low initial dye concentrations, particularly in the case of the most inefficient catalysts (rutile dots). This was interpreted as a reflection of the bimolecular reaction mechanism, the kinetic analysis of which would require knowledge of both the dye concentration and the concentration of surface hydroxy radicals. Nevertheless, for cases in which the concentration of OH⁻ was probably large compared to that of the dye and could be regarded as essentially constant (i.e., for efficient catalysts such as HT-184 and P25), the unimolecular approximation for Langmuir-Hinshelwood analysis provided a satisfactory model of the reaction kinetics.

Among the anatase samples, photocatalytic activity was found to increase with increasing specific surface area and decreasing crystallite size. Ultrasound rutile exhibited minimal activity, even despite its high surface area; this was due to the low adsorptivity and poor hole trapping efficiency generally observed in rutile samples. Thus, this study established that anatase’s typically superior photocatalytic activity is due to inherent
differences between anatase and rutile, rather than effects related to anatase’s usually higher surface area.

The anatase-rutile synergy reported previously for Degussa P25 was confirmed; however, this effect was not observed in laboratory-made ultrafine (D ~ 5 nm) anatase-rutile mixtures, indicating that synergy requires good contact between the two phases as well as an optimal grain size and/or phase composition.

Additionally, it has been demonstrated for the first time that the photocatalytic efficiency of anatase depends critically on particle morphology; specifically, in the anatase nanocrystals with predominantly (1 0 1) surfaces, both the per mass and specific activities calculated in this study were lower than in isotropic anatase particles. This was because the non-dissociative adsorption of water to the (1 0 1) surface minimized the number of surface adsorbed hydroxyl groups that could be converted into hydroxy radicals, which are thought to be essential in photocatalytic oxidation reactions.

If one neglects the role of anatase-rutile synergy, which in this study was ambiguous, then the results obtained in this work collectively indicate that an ideal nanocrystalline TiO₂ photocatalyst should consist of ultrafine anatase particles (D ≤ 10 nm) with high surface area and with a minimum proportion of (1 0 1) surface sites.

Possible future studies include the following: Congo Red photodegradation in the presence of differently sized hydrothermal anatase dots, which would allow an assessment of the surface area dependence of anatase’s activity completely independent of shape effects; photocatalysis experiments using rutile dots with different surface areas; testing mixed-phase powders with different anatase-rutile ratios made using the same general synthetic procedure, so as to determine the optimal phase composition for the
Congo Red reaction; studies of size effects in anatase-rutile mixtures; and computer simulations of Langmuir-Hinshelwood kinetics in which the competitive sorption of \( \text{OH}^\ast \) radicals and dye molecules is quantitatively taken into account.

References


Appendix.

MATLAB code for modeling the growth of monodisperse anatase nanocrystals under hydrothermal conditions

function yprime = anatase_singleNP(t,y);

% LAST UPDATED MAY 29, 2003 BY RAI WAI

% This file contains the equations for the rates of change of the nanoparticle radius and of the bulk monomer concentration. The program treats a system consisting of a fixed number N of identical anatase titania nanocrystals.

% y is a column vector containing the radius of a single nanoparticle (y(1)) and the bulk monomer concentration (y(2)).
% t represents the time elapsed.

% STEP 1: DEFINE AND ASSIGN VALUES TO KNOWN PARAMETERS.

global Ea N gamma T D k0 rhof rhos mu;

% The above global variables can be adjusted by the user in the main Matlab workspace. The units of these variables are:

% Ea: activation energy in J mol^-1
% N: total number of particles; dimensionless
% gamma: surface tension in J m^-2
% T: temperature in K
% D: diffusivity in m^2 s^-1
% k0: preexponential reaction constant in s^-1
% rhof, rhos: fluid and solid densities in g m^-3
% mu: fluid viscosity in g m^-1 s^-1

% The remaining parameters used in the calculations have values that are not altered by the user:

kB = 1.38e-23;       % Boltzmann constant in K^-1
R = 8.314;            % gas constant in mol^-1 K^-1
Vm = 2.08e-5;         % anatase molar volume in m^3 mol^-1
Vsoln = 1e-9;         % total solution volume in m^3
\[\theta = 0.60; \quad \text{%dimensionless constant}\]
\[c_{\text{inf}} = 1 \times 10^{-2}; \quad \text{%very rough estimate of anatase bulk solubility}\]
\[(\text{mol m}^{-3})\]

\[c_l = 2 \times \gamma \times V_m / (R \times T);\]
\[k_s = k_0 \times \exp(-E_a / (R \times T));\]

\[\text{%STEP 2: COMPUTE THE CAPILLARY LENGTH CL AND THE REACTION CONSTANT KS.}\]
\[\text{%STEP 3: COMPUTE THE DAMKOHNER NUMBER DA AND THE DIFFUSION LAYER THICKNESS D, AND THE SINGLE-PARTICLE GROWTH}\]
\[\text{%RATE dr/dt.}\]

\[\text{if } y(1) > 1 \times 10^{-12}\]
\[\text{%Damkohner number}\]
\[D_a = k_s \times y(1)/D;\]
\[\text{%diffusion layer thickness}\]
\[\delta = (2 / (\sqrt{3} \times \theta)) \times \left( (D^2 \times \mu / \rho_f)^{(1/6)} \right) \times \left( (\pi \times \rho_s / (k_B \times T))^{0.25} \right) \times y(1)^{1.25};\]
\[\text{%dr/dt equation}\]
\[y_{p1} = k_s \times V_m \times (y(2) - c_{\text{inf}} \times \exp(c_l/y(1))) / (1 + D_a \times (\delta / (\delta + y(1))));\]

\[\text{%STEP 4: CALCULATE dcb/dt.}\]
\[y_{p2} = -4 \times \pi \times N \times y_{p1} \times (y(1)^2) / (V_m \times V_{sln});\]

\[\text{%STEP 5: Set dr/dt and dcb/dt to 0 once the particles have dissolved so}\]
\[\text{that the program doesn’t have to deal with complex values.}\]
\[\text{else}\]
\[\quad y(1) = 0;\]
\[\quad y_{p1} = 0;\]
\[\quad y_{p2} = 0;\]
\[\text{end;}\]

\[\text{%STEP 6: ODEs expressed as a column vector}\]
\[y_{\text{prime}} = [y_{p1}, y_{p2}];\]