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An Investigation of TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites for Visible Light Photocatalysis

Jeremy Wade
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An Investigation of TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites
for Visible Light Photocatalysis

by

Jeremy Wade

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in Electrical Engineering
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AN INVESTIGATION OF TiO$_2$-ZnFe$_2$O$_4$ NANOCOMPOSITES
FOR VISIBLE LIGHT PHOTOCATALYSIS

Jeremy Wade

ABSTRACT

Environmental pollution on a global scale is expected to be the greatest problem that chemical scientists will face in the 21$^{st}$ century, and an increasing number of these scientists are looking to new photocatalytic systems for the solution. Existing photocatalytic systems are effective for the decomposition of many unwanted organics through the use of efficient semiconductor photocatalysts activated by ultra-violet (UV) irradiation. The demand for visible light activated photocatalytic systems is increasing rapidly. Currently, however, the efficiency and availability of photocatalysts which can be activated effectively by the solar spectrum and especially indoor lighting is severely limited.

The purpose of this project is to investigate the potential of a TiO$_2$-ZnFe$_2$O$_4$ alloyed nanocomposite for use as a visible light activated photocatalyst. An overview of the principles of photocatalysis is first provided. Relevant properties of pure and modified TiO$_2$ are next discussed, and results of studies on structural and photocatalytic properties are presented. Alloyed TiO$_2$-ZnFe$_2$O$_4$ nanocomposites are discussed in detail and their crystal structure, particle size, particle interaction, optical characteristics, and photoactivity are discussed in detail. Measurements characterizing the alloys are carried out using XRD, SEM, EDS, UV-Vis spectroscopy, and photodegradation procedures.
The photoactivity of the alloys is carefully studied through phenol degradation experiments, and recommendations are provided to improve the photocatalysts under investigation.
CHAPTER 1
INTRODUCTION

1.1 History of Photocatalysis

Catalysis can be thought of as an umbrella term to describe any process in which a substance through intimate interaction(s) with the reactant(s) and through a lower energy pathway accelerates an otherwise thermodynamically favored but kinetically slow reaction [1]. Unique processes can be found under the umbrella of catalysis, including photocatalysis, thermal catalysis, acid-base catalysis, redox catalysis, and enzyme catalysis. Photocatalysis in particular has become an increasingly important field and a heavily researched topic by all fields of science, including physicists, chemists, and surface scientists, and is pursued today to solve an ever-widening variety of environmental problems.

The term *photocatalysis* has been used since the 1920s, although the name itself has drawn scrutiny since it incorrectly implies a catalytic reaction driven by light. Photocatalysis, however, broadly defines a photoreaction that is accelerated by the presence of a catalyst. In the mid 1920s, the semiconductor ZnO began attracting attention for use as a sensitizer for the decomposition of both organic and inorganic photoreactions, and TiO$_2$ was soon after investigated for its photodegradation characteristics [2]. Most of the primitive work in semiconductor photochemistry took
place in the 1960s, leading to the first photoelectrochemical cell for splitting water, using TiO₂ and Pt coated electrodes in the early 1970s [3]. In the early 1980s, TiO₂ was used for the first time to sensitize reactions in the photomineralization of selected organics. Since that time, research in the field of photocatalysis has been dominated by studies on the photocatalytic oxidation of organic compounds in water, although there is increased interest in oxidizing bacteria and volatile organic chemicals (VOCs) for the purpose of air purification.

Over the years, many semiconductors with photocatalytic properties have been either thoroughly or partially investigated including TiO₂ (3.2eV), SrTiO₃ (3.4eV), Fe₂O₃ (2.2eV), CdS (2.5eV), WO₃ (2.8eV), ZnS (3.6eV), FeTiO₃ (2.8eV), ZrO₂ (5eV), V₂O₅ (2.8eV), Nb₂O₅ (3.4eV), SnO₂ (3.5eV), as well as many others [4, 5]. Of the semiconductors tested, their uses and applications, if any, vary depending on the individual properties of the photocatalyst. By far, however, TiO₂ has dominated the field of photocatalysis in terms of research, characterization, and applications. The reason for TiO₂’s widespread use comes from its moderate band gap, nontoxicity, high surface area, low cost, recyclability, high photoactivity, wide range of processing procedures, and its excellent chemical and photochemical stability. It should also be noted that TiO₂ is ranked as one of the top 50 most available chemicals, ensuring that it will be around at low cost for quite some time.

One of the greatest advantages of TiO₂ as a photocatalyst is unfortunately also its largest disadvantage. TiO₂ has one stable phase called rutile (tetragonal) and two metastable phases called anatase (tetragonal) and brookite (orthorhombic). Although rutile has a wide variety of applications primarily in the pigment industry, TiO₂’s anatase
phase with a band gap of 3.2eV has proven to be TiO$_2$’s most active crystal structure, largely because of its favorable energy band positions and high surface area. With an indirect band gap of 3.2eV, a photon would need a wavelength equal to or shorter than 385nm to electronically excite this semiconductor, meaning that it needs to be a UV-A or higher energy photon. TiO$_2$’s band gap, although favorable for UV photocatalysis, subjects TiO$_2$ to low efficiency yields in solar applications (its largest potential market) since less than 5% of the sun’s energy is emitted at wavelengths below 385nm. Therefore, whereas the anatase form of TiO$_2$ is considered an ideal photocatalyst for UV applications, in its unmodified form it is rendered highly inefficient for visible light applications.

1.2 Motivation for Visible Light Photocatalysis

Environmental pollution on a global scale is proposed to be the greatest problem that chemical scientists will face in the 21$^{st}$ century and an increasing number of these scientists are looking to new photocatalytic systems for the solution. The photocatalytic process itself will not change; however, a new generation of photocatalysts must be created to utilize the available solar spectrum and not merely the scarcely available UV spectrum. This is a relatively recent objective that has been intensively researched only during the past decade, although interest in the field has been increasing rapidly as can be seen by the magnitude of papers, books, conferences and available applications that are being devoted to (and because of) the topic.

Visible light photocatalysis is currently being pursued across the globe, including research groups from countries such as Japan, China, France, South Korea, United States,
United Kingdom, Germany, Canada, Italy, and Taiwan, among others. Even though the current success of these photocatalysts has been limited (as discussed further in Chapter 2), both the immediate and long-term applications are in high demand. Table 1.1 lists current research topics and applications of visible light photocatalysis, all of which use the semiconductor photocatalyst TiO$_2$ for a primary role in the system.

Table 1.1 Desired Applications of Visible Light Photocatalysis [6,7].

<table>
<thead>
<tr>
<th>Visible Light Photocatalysis Research Topics</th>
<th>Phase of Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water splitting for hydrogen production</td>
<td>Research</td>
</tr>
<tr>
<td>Self-cleaning films (mirrors, windows, etc.)</td>
<td>Currently in use</td>
</tr>
<tr>
<td>Self-cleaning structures (cement, aluminum building materials, marble statues, sound proof walls, tents, lamps, etc.)</td>
<td>Currently in use</td>
</tr>
<tr>
<td>Self-cleaning coating materials for cars</td>
<td>Research</td>
</tr>
<tr>
<td>Air purification systems for destruction of bacteria, viruses, spores, VOCs</td>
<td>Currently in use</td>
</tr>
<tr>
<td>Water purification</td>
<td>Currently in use</td>
</tr>
<tr>
<td>Antibacterial textile fibers</td>
<td>Currently in use</td>
</tr>
<tr>
<td>Oil spill cleanup</td>
<td>Currently in use</td>
</tr>
</tbody>
</table>

1.3 Project Goals

Research and the pursuit of an optimal visible light activated photocatalyst are trailing behind the desired and often mandatory applications that are growing exponentially. Although modified TiO$_2$ that can be activated by short wavelength visible light is currently available, there are numerous drawbacks (discussed in Chapter 2) that
prevent these catalysts from dominating the coveted market. The ideal visible light activated photocatalyst will need to meet several basic criteria (Sections 1.3.1-1.3.4), each of which can be met with successful completion of the project objectives.

1.3.1 Capability of Visible Light Activation

Visible light is typically described as the portion of the electromagnetic spectrum with wavelengths between 400nm and 700nm (sometimes defined more broadly as 380-780nm). For solar applications, even pure TiO$_2$ shows slight photoactivity since approximately 3.5% of the sun’s irradiation corresponds to UV-A wavelengths between 300 and 380nm. If the band gap of TiO$_2$ or another efficient photocatalyst can be reduced, lower energy photons may be absorbed by the catalyst and the photoactivity of the catalyst could increase roughly proportional to the increase in the absorbed solar spectrum. Theoretical limits relating to redox potential levels exist, however, for the extent to which wavelengths can be absorbed while still maintaining efficient photocatalysis. For instance, the valence band edge of the semiconductor photocatalyst must have sufficient energy to stimulate the oxidation reaction needed for the generation of radicals (further discussed in Chapter 2). If the band gap is lowered beyond a specific point, the energy requirements of the photocatalytic reaction will not be met, although the semiconductor maintains visible light absorption. The band gap of the ideal photocatalyst should therefore be as small as possible while still meeting the minimum requirement as governed by the semiconductor’s band edge energy levels.
1.3.2 Photochemically Stable

Stability is a critical factor in photocatalytic reactions. Metal sulfide semiconductors, for instance, although having a desirably small band gap, are susceptible to photoanodic corrosion due to the energetically unfavorable position of their valance band edge. The photocatalytic lifetime of these semiconductors is therefore extremely short, where the exact time depends on the reaction environment. Other catalysts such as ZnO are suitable photocatalysts for various UV applications, although this semiconductor undergoes photocathodic corrosion when in aqueous solutions, eliminating it as a potential catalyst for many applications. The ideal photocatalyst should be photochemically stable and therefore insusceptible to any type of corrosion in all reaction environments.

1.3.3 Nontoxic

Since the nature of photocatalytic reactions are usually involved with some form of environmental purification (water, air, etc.), it is considered counterproductive to use toxins such as carcinogens as a means for purification. The largest impact the problem of toxicity has on the field of visible light activated photocatalysis is related to the semiconductor CdS, which is a known carcinogen, mutagen, and irritant. CdS, although unfavorable because of its quick electron-hole pair recombination times, is considered ideal as far as energy band edge positions are concerned. Its band gap (2.5eV) is small enough to absorb wavelengths corresponding to green light and large enough to have energy bands that deter corrosion. TiO$_2$, on the other hand, has been considered environmentally friendly, adding to its appeal as a photocatalyst. TiO$_2$ has been used in
applications involving both direct and indirect contact with humans with negligible
associated health risks. The ideal photocatalyst will be nontoxic, posing imperceptible
health concerns in all environments.

1.3.4 Cost Effective

The cost of the photocatalyst is a major factor in determining the feasibility of an
application, whether it is a photocatalyst-coated light bulb for air purification or a large-
scale water purification station. The most promising visible light photocatalyst to date is
TiO$_2$ implanted with metal ions. The ion implantation process for increasing the visible
light photoactivity of TiO$_2$ has earned the name 2$^{nd}$ generation photocatalysis by some of
the most distinguished researchers in the field. This 2$^{nd}$ generation photocatalyst,
however, does not come without a price. The ion implantation process has an overhead
often exceeding $500,000 depending on the size and type of process. It also requires
extensive training of operators and has the disadvantages of low surface areas for
treatments. This means that large-scale productions would require extensive time and
small-scale productions would not be able to provide the overhead capital needed. An
ideal photocatalyst would have a low-cost preparation technique that is highly repeatable
and has the feasibility for large-scale production.
CHAPTER 2

PRINCIPLES OF PHOTOCATALYSIS

2.1 Principles of Photocatalysis

Photocatalysis can be defined as the acceleration of a chemical reaction by either direct irradiation or by the irradiation of a catalyst that in turn lowers the activation energy for the primary reaction to occur. Photocatalytic oxidation (PCO), also known as heterogeneous photocatalysis, has been used since the mid 1970s to decontaminate water from harmful microorganisms and throughout the past decade has been applied to compensate for insufficiencies in spore destruction and decontamination in ultraviolet germicidal irradiation (UVGI) air disinfection systems.

In a heterogeneous photocatalytic process, photoinduced chemical reactions or molecular transformations occur at the surface of a catalyst. This general process can be further divided into catalyzed or sensitized photoreactions based upon whether the initial excitation occurs at the surface of the adsorbate molecule or the catalyst [8]. A catalyzed photoreaction occurs when the initial photoexcitation occurs in an adsorbate molecule, which then reacts with a catalyst substrate. A sensitized photoreaction occurs when the initial photoexcitation occurs in the catalyst substrate and then energy transfer, which is often in the form of electron transfer, takes place with a ground (non-energetically excited) state molecule.
2.2 Principles of Photocatalytic Reactions

In general, a sensitized photocatalytic oxidation process is one in which a semiconductor upon absorption of a photon of suitable energy can act as a photocatalytic substrate by producing highly reactive radicals that can oxidize organic compounds. A molecular description of a general photocatalytic process is given below in Equations 1-6 [9]. For example, the most commonly used and researched semiconductor catalyst, TiO$_2$, is used as the substrate, and H$_2$O and O$_2$ are used as adsorbates.

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow \text{TiO}_2 (e_{cb}^- + h_{vb}^+) \\
\text{TiO}_2 (e_{cb}^- + h_{vb}^+) & \rightarrow \text{TiO}_2 + \text{heat} \\
\text{TiO}_2 + \text{H}_2\text{O}_{ads} & \rightarrow \text{TiO}_2 + \text{OH}^- + \text{H}^+ \\
e_{cb}^- + \text{O}_{2ads} & \rightarrow \text{O}_2^- \\
h_{vb}^+ + \text{OH}^- & \rightarrow \text{OH}^- \\
\text{OH}^- + \text{Organics} & \rightarrow \text{H}_2\text{O}, \text{CO}_2, \text{etc.}
\end{align*}
\]

One point that should be obvious from Equations 3-6 is that a photocatalyst’s interaction with other adsorbed molecules is essential. Photoactive semiconductor surfaces can attract electron donors and acceptors through both chemical and electrostatic forces including van der Waals forces, induced dipole-dipole interactions, dipole-dipole interactions, hydrogen bonding, outersphere complexation, ion exchange, surface organic matter partitioning, and sorbate hydrophobicity.
2.3 Band Gap Excitation

Equation 1 suggests that the theory behind photocatalysis relies on rudimentary semiconductor principles. When a photocatalyst is irradiated with photons with energies greater than that of the semiconductor’s band gap, $E_g$ (eV), an electron is transferred to the conduction band, leaving behind a positive hole in the valence band. The pair of photoexcited charges that occurs within a particle is called an electron-hole pair (EHP). The energy required of a photon to generate an EHP in a photocatalyst can be related to its wavelength by:

$$\lambda \text{ (nm)} \leq \frac{1240}{E_g}$$

(7)

The efficiency of a photocatalyst is measured in terms of the number of reactions occurring per photon absorbed, which depends on the rate of the generation, fate of migration, and energy levels of the photoexcited EHPs. The rate that EHPs are generated is determined first by irradiation conditions such as photon energies and fluxes, and secondly by optical absorption characteristics of the photocatalytic particles such as their band gap, size, and surface area. The fates of the EHPs determine the reactions that occur both within the particle and on its surface.

Figure 2.1 shows several of the possible reaction pathways that can be taken by EHPs once they are generated by irradiation of suitable energy. Reaction 1 is the generation of an EHP upon absorbance of a single photon with an energy greater than the band gap of the semiconductor. Reactions 2-6 depend on bulk and surface properties of the photocatalyst particle. Reactions 2 and 3 can be respectively described as volume and surface recombination and are the dominant fate of EHPs, leading to low photocatalytic efficiencies. The frequency of these recombination processes can be decreased by
reducing the particle size (although EHP recombination begins to increase again near quantum sizes), increasing crystallinity of the lattice (reducing surface and bulk defects and impurities), and/or increasing the transfer rate of charges by preadsorbing reactant species on the surface [8]. Reaction 4 is referred to as “charge trapping” and can occur in localized energy levels in the band gap region. Charge carriers that become trapped in these energy levels eventually decay slowly by bimolecular and geminate recombination on the order of micro or nanoseconds, depending on the properties of the traps [10]. Reaction 5 occurs when an electron acceptor is reduced by removing a migrating electron from the surface of the particle. Reaction 6 is an oxidation reaction that occurs when an electron from a donor species combines with a hole that has migrated to the surface.

![Possible Reaction Pathways for Photogenerated EHPs](image)

**Figure 2.1 Possible Reaction Pathways for Photogenerated EHPs [8].**

### 2.4 Band Edge Positions

The energy of a semiconductor’s band gap is equal to the difference in energy between the conduction band edge and the valence band edge. Knowledge of band-edge
positions is useful when creating and analyzing semiconductor photocatalysts because they indicate the thermodynamic limitations for the photoreactions that can be carried out by the charge carriers. For example, if the oxidation of an organic compound is desired by the photocatalyst, then the valence band edge of the semiconductor must be positioned favorably relative to the oxidation potential of the organic compound. On the other hand, if the reduction of a molecule such as O₂ is required, then the conduction band edge of the semiconductor must be positioned favorably relative to the reduction potential of the O₂ molecule.

The band gaps of most semiconductors are well known; however, the respective energy levels of the valence (Eᵥ) and conduction bands (Eₓ) have not been accurately determined for many of these same semiconductors. For those semiconductors where the band energies have not been determined experimentally (usually through flatband potential measurements in contact with aqueous solutions of known pH), the values of Eᵥ and Eₓ can be determined by a simple relationship if a semiconductor’s band gap (E₉, units of eV) and absolute electronegativity (-χ, units of eV) are known, where the absolute electronegativity is essentially Fermi level of a pristine semiconductor [4]:

\[ E_c = -\chi + 0.5 \cdot E_g \]  \hspace{1cm} (8)
\[ E_v = -\chi - 0.5 \cdot E_g \]  \hspace{1cm} (9)

Figure 2.1 shows the band-edge positions of several dominant photocatalysts in relation to the oxidation and reduction potentials of H₂O. It should be noted that, although the bulk electronic structure of the semiconductor photocatalysts changes only faintly with pressure and temperature, the pH of the electrolyte used during the study has a direct
effect on the flatband potential and therefore proportionally on the band-edge positions. As a result, the potentials shown in Figure 2.1 can vary slightly.

![Diagram of Band-edge Energy Levels for Commonly Used Photocatalysts](image)

Figure 2.2  Band-edge Energy Levels for Commonly Used Photocatalysts.

The energy positions of the band edges are shown both on the absolute vacuum scale (AVS) and with respect to the normal hydrogen electrode (NHE) and can be related by

$$E_{\text{AVS}} = -E_{\text{NHE}} - 4.5 \ .$$

Quantum size (Q-size) effects also must be considered when determining electronic properties of semiconductors such as the energy positions of the valence and conduction band edges. Quantum effects occur when the size of the semiconductor particle is close to or smaller than the Bohr radius of the first excitation state [11],
causing the particle to possess properties characteristic of both its bulk and molecular phases. Quantum effects are common for colloidal solutions and particles with sizes close to or smaller than 10nm (the actual size range is widely debated), which is important since the size range of optimal TiO$_2$ nanoparticles for photocatalytic reactions has been found to be between 10-20nm. The most dramatic influence of Q-size effects is that it can be used to tailor the band gap and band-edge positions of Q-size semiconductor nanoparticles for sensitive applications. As a nanoparticle’s size decreases, its band gap increases primarily with an increase in conduction band energy levels and also a slight decrease in valence band energy levels [12]. Studies on quantum sized TiO$_2$ have suggested a 0.15eV band gap increase relative to bulk anatase TiO$_2$ and a 0.10eV band gap increase relative to bulk rutile TiO$_2$ [13]. Based on such experiments, it has been concluded that precision of a particle’s size can aid in promoting (or possibly inhibiting) a redox or sensitization reaction that would not be possible by the same particle of larger diameter.

2.5 Electron-Hole Pair Recombination

Although charge transfer to adsorbate species is the desired fate of electron-hole pairs (EHPs), the vast majorities recombine, creating a loss in photocatalytic efficiency often greater than 90%. This recombination process between the photoexcited electron and hole can occur either in the volume of the semiconductor particle or on the surface of the particle with a byproduct of heat release (Equation 2) [8]. The EHP recombination process itself results when the electron-hole recombination time is shorter than the time it takes for the carrier to diffuse to the surface. Femtosecond and picosecond transient
absorption and emission spectroscopy measurements studying charge carrier trapping and recombination kinetics in semiconductors such as TiO$_2$ have estimated electron trapping times around 20-200fs and the mean lifetime for EHPs to be in the range of 30ns. It is generally accepted, however, that EHP recombination occurs on both a picosecond and nanosecond time scale, depending on the semiconductor and its particle size [14-16]. In general, as the size of the particle decreases approaching approximately 10-15nm, EHP recombination decreases since the diffusing charge carriers can quickly reach the surface of the particle. If the particle size decreases below this optimal particle size leading to quantum sizes, however, EHP recombination again increases due to the close proximity of the charges [17]. Other factors such as substitutional impurities, lattice defects, and vacancies, which can serve as electron traps near the surface or in the bulk, also affect EHP recombination rates since they provide possible alternative pathways for the photogenerated electrons to recombine with holes.

### 2.6 Role of Photogenerated Electrons in Photocatalysis

For a semiconductor to have a high quantum efficiency, its photoinduced charges must freely migrate to the surface of the particle so that they can participate in reactions with adsorbed species. The migration of electrons to the surface is not only in competition with EHP recombination but also with trapping by coordination defects at the surface and by lattice defects in the particles bulk. The photogenerated electrons that are able to migrate to the surface are primarily used in the reduction of O$_2$ (in both aqueous and gas solutions), other reactive species such as the superoxide radical O$_2^-$ (Equation 4) or the singlet oxygen, which can in turn stimulate other radical chain
reactions involving H$_2$O$_2$ or O$_3$ [18]. Experiments have proven that the photocatalytic ability of TiO$_2$ is almost completely suppressed in the absence of an electron scavenger to prevent EHP recombination [19]. This may be one possible reason for the negligible photoactivity in many rutile phase TiO$_2$ particles which have a conduction band energy just below that required to reduce molecular oxygen.

2.7 Role of Photogenerated Holes in Photocatalysis

The positively charged photogenerated holes that are able to migrate to the surface can either directly oxidize organic species with lower oxidation potentials or they can create the highly reactive and short-lived hydroxyl radical $^\cdot$OH upon the catalyst’s adsorption of H$_2$O (Equation 5). The adsorption of H$_2$O on the surface of TiO$_2$ is an active and debated area of research, although it is commonly accepted that H$_2$O is adsorbed both molecularly and dissociatively [20]. In both molecular and dissociative adsorption of H$_2$O on the surface of TiO$_2$, a probable evolution path is for the localized hole states exposed on the surface to transfer directly to other species where direct oxidation can occur. Dissociative adsorption can have the extra benefit of forming a hydroxyl radical that can desorb from the surface to oxidize organic species [21].

2.8 Photocatalytic Oxidation of Organics

The transcendent purpose of heterogeneous photocatalysis is to decompose organics that are harmful to humans and the environment. Photocatalytic oxidation processes (PCO) are able to replace many customary disinfection methods including
ozonation, chlorination, and intense UV-C irradiation, which are potentially dangerous and often create biologically harmful by-products.

Examples of organic compounds that have successfully been decomposed into CO₂ and harmless minerals by photocatalysis include phenols, halophenols, haloalkanes, alkanes, aromatics, cresols, alcohols, polymers, surfactants, herbicides, pesticides, dyes, bacteria, viruses, fungi, molds, cancer cells, and highly resistant spores [2]. The basic mechanism for the decomposition of organic compounds is the same, although variations exist in the photocatalyst characteristics that are critical to the reaction such as the number and strength of surface acid sites and the redox potentials of the photocatalyst relative to that of the organic and inorganic reaction species.

In addition to the strong oxidation characteristics of a PCO process, a second advantage it provides for environmental purification and disinfection purposes is that most photocatalysts can be made either in powder or thin-film formations. Although the preparation procedures and many properties vary among the two formations, each is beneficial to decomposing organic degradants on an application level. Nanoparticle photocatalysts, for example, are often easier to create with high efficiencies and can be implemented in mixed aqueous solutions and even woven into fibers for an intimate and consistent interaction with organics. Films have the advantage of avoiding catalyst filtering processes required after a photocatalytic reaction is complete and are therefore beneficial in applications such as water purification and bacteria destruction.
CHAPTER 3

TiO$_2$ PHOTOCATALYSIS

3.1 Current UV Activated Photocatalysis

Commercialized TiO$_2$ is the dominant semiconductor found in practical applications of UV activated photocatalysis, and countless laboratories throughout the world continue to focus on modifying TiO$_2$ in attempts to address an endless list of environmental concerns that may be solved through photocatalysis. An increasing number of major companies including Degussa, Aldrich, and Merck are marketing both modified and pure TiO$_2$ for research and application oriented groups. Of these companies, Degussa has produced a catalyst named Degussa P-25 TiO$_2$ that is commonly used as an “ideal” photocatalyst for UV-stimulated applications and as a reference for research laboratories worldwide. Degussa P-25 TiO$_2$ is created in powder form by flame hydrolysis of TiCl$_4$ at temperatures in excess of 1200°C in the presence of O$_2$ and H$_2$ and then treated with steam to remove the residual HCl. The finished product is greater than 99.5% pure TiO$_2$ with small amounts of impurities such as SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$. The anatase to rutile ratio is approximately 70:30 with a mean surface area of 50m$^2$/g and average particle size of 21nm [22]. Although Degussa’s TiO$_2$ has found worldwide applications because of its remarkable photoactivity that is attributed to its crystallinity,
surface area, and moderate purity, research groups continue to create modified catalysts that have increased performance under UV irradiation conditions.

The primary focus of research groups working on UV activated photocatalysis is to increase the quantum yield of the photocatalytic process, which can be accomplished using either one (or a combination) of two general methods. The first method deals with optimizing the structure of pure TiO$_2$, and the second method deals with surface modifications on TiO$_2$, usually in the form of doping.

**3.1.1 Increasing the Photoactivity of Pure TiO$_2$**

On a general level, there are three rudimentary parameters that affect the photocatalytic activity of any photocatalyst including TiO$_2$: its light absorption spectrum and coefficient, the rate of redox reactions that occur at its surface, and the rate or probability of EHP recombination within the semiconductor [23]. On a more defined level, there are numerous factors that intimately govern the three parameters above, including a catalyst’s band gap, surface area, porosity, crystal structure, crystallinity, purity, density of surface hydroxyl groups, e$^{-}$ and h$^{+}$ migration characteristics, surface acidity, and size distribution. Each of these characteristics can be improved or compromised using an extensive list of chemical [5, 24] and mechanochemical [25, 26, 27] synthesis techniques used to create photocatalytic materials, although optimizing several of these characteristics have demanded more attention than others.
3.1.1.1 Optimizing Particle Size

A significant emphasis has recently been placed on optimizing the particle size of pure TiO₂ for various photocatalytic processes. This is largely due to the fact that the particle size of the catalyst directly affects properties critical to photoactivity such as surface area, while indirectly affecting other properties such as EHP recombination, redox potentials [12], crystal structure (at specific thermal conditions) [28], and even absorption characteristics [29, 30]. The optimal particle size of anatase TiO₂ with regards to photocatalytic activity has been confined to a range of several nanometers according to experiments reported in literature that use various organics as test degradants [17, 31, 32]. A commonly accepted rule is that the photocatalytic activity of TiO₂ increases as the diameter of an anatase particle decreases until it reaches sizes of approximately 10-15nm. When the particles diameter decreases to ranges between 6-9nm, photocatalytic activity has been found to slightly decrease.

The theory behind an “optimal particle size” for a TiO₂ particle has been investigated and revealed through EHP recombination studies [33]. It has been found that volume recombination of charge carriers is the dominant process in large TiO₂ particles, whereas surface recombination is dominant in particles approaching quantum sizes. As the diameters of large particles are reduced, recombination can be reduced due to a decreasing distance required for the migration of charge carriers to the surface. A reduced particle size also coincides with increased surface area. The increased number of active sites on the surface of the photocatalyst translates into a faster rate of e⁻ and h⁺ reactions with surrounding substrates. As the diameters of the particles are decreased further towards quantum sizes, the photoactivated electrons and holes excite relatively
close to the surface of the particle. Surface EHP recombination becomes dominant in these quantum sized particles since it is characteristically faster than the interfacial charge carrier process [34]. Thus the “optimal particle size” for TiO$_2$ nanoparticles is the diameter at which surface area is maximal, while the particle is still large enough to avert quantum effects.

3.1.1.2 Optimizing Crystal Structure

Optimizing the crystalline phase of pure (as well as modified) TiO$_2$ has also attracted a considerable amount of attention in the field of UV photocatalysis. As discussed, TiO$_2$ crystals can be formed in one of three polymorphs named rutile, anatase, and brookite. Of these three, rutile is the only stable phase, while the other two metastable phases irreversibly transform into rutile upon heating. Brookite, the least studied phase of TiO$_2$, is known to be less photoactive than anatase [35], exhibits many of the same material characteristics of rutile, and possesses a band gap of approximately 3.4eV [36]. Brookite is rarely found in significant concentrations; therefore, pure anatase and rutile as well as their transition phases are usually studied. A phase equilibrium does not exist for the anatase-rutile transformation; therefore, no specific temperature can be assigned to the phase transition, which depends on parameters such as synthesis method, reaction atmosphere, impurity content, particle size, and the oxygen vacancy concentrations within the TiO$_2$ lattice [37].

Both the anatase and rutile crystalline phases are characterized by the tetragonal crystal system, and the difference in their structure lies in the assembly of their octahedral chains, causing them to differ in particle morphology and therefore in chemical and
physical properties. Theses differences include surface area, surface charge separation and recombination, formation of intermediates, photoadsorption and photodesorption of oxygen, and the adsorption of water and hydroxyl groups [38]. It is these differences, not simply just the crystal structure variations, which favor the anatase form of TiO$_2$ in photocatalytic reactions. Various studies have shown the advantages of anatase crystals, such as the larger band gap of anatase favoring redox reactions, faster EHP recombination on the surface of rutile particles [39], and larger surface area of anatase powders due to decreased particle size [40]. It is therefore commonly accepted that the anatase crystal structure is the most photoactive phase of TiO$_2$ and that the rutile content therefore is usually eliminated or significantly reduced. It is possible, however, that an interaction between highly optimized anatase and rutile particles may provide a synergistic photocatalytic effect due to increased efficiency in charge separation, using a sensitization method where photoexcited electrons are transferred from the conduction band of an anatase particle to the lower energy conduction band of a rutile particle [38, 41-44].

3.1.2 Increasing the Photoactivity of TiO$_2$ through Surface Modifications

Selective surface treatments are often employed in TiO$_2$ photocatalysts to enhance the photoactivity through the reduction of EHP recombination and thus the enhancement of interfacial charge transfer. Although numerous surface modification techniques have been implemented, the most common has been through the doping of TiO$_2$ with noble metals and transition metal ions. It has been found that doping TiO$_2$ with metals in
concentrations less than two mole percent can have a variety of effects on the electronic properties, structure, and thermal stability of TiO$_2$ [19].

Studies have been conducted for various applications using the majority of metals from the alkali, alkaline, transition, and lanthanide groups of elements and even metalloids such as Sb. Of these metals, several have been proven to increase the photoactivity of TiO$_2$, providing the correct concentrations and particle interactions. Experiments reported in literature (although often conflicting) have shown that doping with lanthanides increases the photoactivity of TiO$_2$ in the general decreasing order of Gd, Nd, La, Pr, Er, Ce, Sm [45], and doping with transition metals increases the photoactivity in the general decreasing order of Pt, Fe, Ni, Au, Pd, Cr, Ag [46, 47]. There exist several variables that prevent a concise, ordered, and even possibly accurate list of how dopants affect the photoactivity of TiO$_2$, including the preparation procedure of the photocatalysts, the particle’s size, and the degradant used to study photocatalysis. Research has been found that the photocatalytic efficiency typically increases with metal loading because of reduced EHPs, and then above a certain concentration (varying on metal dopant and preparation technique) the efficiency begins to decrease as the dopants begin to act as recombination centers. The optimum doping concentration in most cases has been found to be between 0.8-1.2mol%, although some metals decrease catalytic efficiency in any concentration. In fact, selected metal ions such as Al$^{3+}$ are commonly used to suppress the photoactivity of TiO$_2$ used in the pigment industry.

It should also be noted that some researchers claim band gap reductions in TiO$_2$ through chemical doping of metal ions based on UV-Vis spectroscopy studies. This is a debated assumption, since metal ions through chemical methods (all using low
calcination temperatures) such as precipitation, sol-gel, and reverse micelles, typically modify only surface properties of TiO$_2$ particles and not the bulk structure [23]. It should be noted however, that the sensitized heterogeneous photocatalysis occurs at the surface and therefore the surface properties are inherently as important as that of the bulk structure in many respects. Since TiO$_2$ nanoparticles with diameters between 10 and 20nm are often used in metal ion doping, however, claims have been made that Ti$^{4+}$ ions may be isomorphically replaced by metal ions with small ionic radii, possibly reducing the bandgap of TiO$_2$ by the overlapping of orbitals [48].

The doping and impregnation of non-metals have shown perhaps the most remarkable effects on the surface properties of TiO$_2$ and have been drawing an increasing amount of experimental studies. TiO$_2$ particles impregnated with SO$_4^{2-}$ ions have proven to form S=O and O-S-O bonds on the surface of the TiO$_2$ particles, therefore modifying its electronic environment [49]. This alteration on the surface of TiO$_2$ particles leads to increased surface acid sites, increased surface area, smaller grain sizes, and increased stability of the anatase crystal structure, all of which are critical for photocatalytic performance. The substitutional doping of small amounts of nitrogen for oxygen in the TiO$_2$ lattice has also shown notable changes in the photoactivity of TiO$_2$. Unlike sulfur with a large ionic radius, nitrogen has an ionic radius comparable in size to oxygen and therefore can be incorporated into the TiO$_2$ lattice [50], which not only leads to increased photocatalytic efficiencies, but also extends electronic properties of the TiO$_2$ and will be discussed more in the following section.
3.2 Current Visible Light Activated Photocatalysts

The trend of TiO$_2$’s use in both research labs and new photocatalytic technologies suggests that it will be at the forefront of the expanding field of visible light photocatalysis in upcoming years, despite certain unfavorable properties it possesses. A general thought among research groups pursuing the future of photocatalysis is that it will be easier to alter or confront TiO$_2$’s unfavorable properties instead of researching an alternative list of semiconductor photocatalysts that in itself is extensive and perhaps partially exhausted. For these reasons and others, TiO$_2$ has in the past and is currently being used as the dominant catalyst in most visible light photocatalytic studies.

As mentioned, the three basic parameters that broadly govern a semiconductor’s photocatalytic activity are: its light absorption properties (spectral absorption and coefficient); rate of oxidation and reduction reactions occurring at the surface; and the rate of EHP recombination. In the quest for a highly efficient visible light activated photocatalyst, all of these three parameters must be taken into consideration, and the first two have to be directly modified. It is important to note that, unlike research on UV activated photocatalysis, which attempts to increase the quantum yield of the photocatalytic reaction, research on visible light activated photocatalysis attempts to extend the photoactivity of a catalyst to longer wavelengths.

3.2.1 Ion Implantation

Ion implantation is a process in which high energy ions bombard and penetrate a surface, interacting with the substrate atoms below the surface. The most common application of ion implantation is the doping of semiconductors to create charge carriers
within the lattice and therefore altering the semiconductor’s electronic properties. The key advantage of this experimentally repeatable method when working with nanoparticle substrates such as TiO$_2$ is that the catalyst’s bulk can be selectively modified and not merely the surface properties as with chemical synthesis techniques.

The ion implantation process has been used to dope TiO$_2$ with metal ions such as Li, Mg, Al, Hg, K, Ca, V, Mn, Fe, Ni, Zn, Ge, Sr, Zn, Nb, Mo, Ru, Rh, Cd, Sn, Sb, Ba, W, Pb, Bi, Ti, and Cr [5]. Many of these metal ions show no photocatalytic improvement over pure TiO$_2$ and can be characterized by only humble red-shifts in absorbance measurements, whereas others such as Cr and V exhibit smooth absorbance shifts into the visible region [6]. This fact suggests that it is not the ion implantation process itself that is beneficial for extending the photoactivity of TiO$_2$ into the visible region, but the incorporation (whether substitutionally or interstitially) of specific ions with intricate properties in the bulk of the TiO$_2$ lattice.

The most common ion implantation procedures reported in literature for doping TiO$_2$ uses Cr ions in concentrations ranging from 2-26mol/g implanted by a 150keV ion accelerator [51]. The absorbance region proved to be red-shifted roughly proportional to the doping concentration, with absorbance regions exceeding 550nm. Photocatalytic studies have proven successful for the decomposition of NO under visible light irradiation, and various formations of photocatalysts have been tested including both powders and films. The recent successes of ion implantation in the field of visible light photocatalysis have merited the technique the title second-generation TiO$_2$ catalysis.

In spite of the promising results that have been reported on ion-implanted TiO$_2$, the feasibility of cost-effective applications of any considerable size is still disputed. The
overhead cost of the ion implantation process is considered a significant burden to overcome for anyone except large-scale manufacturers of modified TiO\textsubscript{2}, which means that a respectable-sized market must first exist. Further experiments also need to be conducted to support claims of photoactivity at wavelengths in excess of 550nm. Current photoactivity conclusions are based on wideband visible light sources and diffuse reflectance plots where the trailing wavelengths of absorbance curves are given credit for photoactivity.

### 3.2.2 Synthesization Techniques

Synthesization between the interfaces of two semiconductors takes place when interparticle charge transfer occurs from one particle to another through a natural difference in energy band levels. Synthesization is applicable to the field of visible light photocatalysis when an ordinarily non-photoactive small band gap semiconductor is used to synthesize a larger band gap semiconductor. To date, the most common semiconductor coupling systems employing photosensitization are TiO\textsubscript{2}-CdS and ZnO-CdS nanocomposites.

CdS with a band gap of 2.5eV is almost invariably used as the synthesizer for large band gap semiconductors because of the ideal positions of its conduction and valence band edges. Being a sulfide, its conduction band edge is inherently slightly more negative (referencing the NHE scale) than most wide band gap oxides, and its valence band edge is energetic enough for oxidation reactions required of photocatalysis. CdS alone, however, shows little or no signs of photoactivity because of both its instability and its rapid EHP recombination rates. Studies have proven that with the proper particle
interaction, CdS-TiO$_2$ nanocomposites can efficiently decompose organics such as phenol and methylene blue under visible light irradiation less than approximately 495nm [52].

The reaction as shown in Figure 3.1 occurs when a CdS particle is excited by a photon with a wavelength less than 495nm. An EHP is formed, and the photogenerated electron is quickly transferred to the conduction band of a coupled TiO$_2$ particle that has a conduction band edge approximately 0.5eV more positive than the CdS particle, thus providing an energetically favorable reaction. The photogenerated hole in the often quantum–sized CdS particle can theoretically migrate to the surface and participate in the oxidation of adsorbed organics. The electrons that are transferred to the conduction band of TiO$_2$ have no holes to recombine with and therefore participate in reduction reactions according to the conduction band energy level of TiO$_2$, since the electron has already lost part of its initial energy in transferring from CdS.

![Figure 3.1 TiO$_2$-CdS Synthesization Reaction Mechanisms.](image)
Several properties must be carefully controlled in current synthesized photocatalytic reactions. First, the size of the nanoparticles must be carefully controlled. If the TiO$_2$ exhibits quantum effects, its conduction band edge will approach the energy level of the coupled CdS particle conduction band, providing lower electron transfer rates and drastically decreasing photocatalytic efficiencies [53]. Secondly, CdS is known to be a light-sensitive material and can decompose under irradiation when interacting with O$_2$ [52]. It is possible that the decomposition reaction of CdS into Cd$^{2+}$ may decrease upon synthesis with TiO$_2$; however, repeated use of the coupled system is perhaps hindered.

The promising results of synthesized TiO$_2$-CdS photocatalysts have been primarily hindered by the toxicity of CdS and its label as a known carcinogen, which obviously doesn’t coincide with the environmental applications required of photocatalysis. Synthesized photocatalysts may one day gain more respect when stable and nontoxic photocatalyst can be found to replace CdS.

3.2.3 Non-Metal Dopants

Perhaps the most recent efforts to discover visible-light activated photocatalysts have been made in the substitution of non-metals such as N, C, S, P and B for oxygen sites in the TiO$_2$ lattice. Of the various non-metals, nitrogen is most frequently used for studies as can be seen by the expanding number of publications. In just the past year, visible light photocatalytic degradation studies have been conducted on N doped TiO$_2$ using methods such as spray pyrolysis [54], sputtering [55], pulsed laser deposition [56], sol-gel [57], and mechanochemistry techniques [57], among others.
Nitrogen-doped TiO\textsubscript{2} (TiO\textsubscript{2-x}N\textsubscript{x}) is accomplished by substitutionally introducing nitrogen atoms into oxygen vacancy sites in the crystal structure of TiO\textsubscript{2}, although it has been debated as to whether the visible light photocatalytic activity can be attributed to substitutionally doped nitrogen atoms or oxygen vacancies stabilized by nitrogen doping. Publications have suggested band gap reductions for TiO\textsubscript{2-x}N\textsubscript{x} photocatalysts to be around 2.9-2.7eV, with valence and conduction band energy level alterations [55].

### 3.2.4 Semiconductor Coupling

Research on the coupling of semiconductor photocatalysts as nanocomposite alloys has taken place for more than a decade, although many questions still exist as to the interaction mechanisms between the particles. There is little doubt that the effectiveness of the coupling of nanoparticle semiconductor photocatalysts is due at least in part to interfacial charge transfer between two different semiconductors with disparately favorable band edge energy levels.

The band gaps and energy band levels for most metal oxides and sulfides have been provided in literature. Low band gap sulfides and selenides, including CdS, CdSe, FeS\textsubscript{2}, and RuS\textsubscript{2} have been investigated as synthesizers for wide band gap photocatalysts such as ZnO and TiO\textsubscript{2}. These coupled semiconductors have portrayed optimistic photocatalytic activity under visible light irradiation; however, they are plagued with unfavorable characteristics such as toxicity and susceptibility to photoanodic corrosion. TiO\textsubscript{2} combined with wide and narrow band gap metal oxides (both semiconductors and insulators) have also been investigated, including WO\textsubscript{3}, MoO\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, SnO, CuO, CeO\textsubscript{2}, V\textsubscript{2}O\textsubscript{5}, Al\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, and...
ZnFe$_2$O$_4$. These alloys have largely been used for the UV activated photocatalytic enhancement of TiO$_2$ or for other properties relating to optics or sensors applications.

TiO$_2$, alloyed with ferric-based semiconductors such as Fe$_2$O$_3$ and ZnFe$_2$O$_4$, have drawn particular attention in the field of visible light photocatalysis, primarily for ferrous semiconductors ability to absorb visible light with wavelengths shorter than 563nm and 652nm respectively, while not being sensitive to photoanodic corrosion. Although Fe$_2$O$_3$ and ZnFe$_2$O$_4$ nanoparticles exhibit photocatalytic properties, the reducing power of their photo-generated electrons have insufficient energy for the reduction of O$_2$, which is the primary electron scavenger in most photocatalytic reactions. This characteristic suggests that visible light photocatalysis using ferric-based semiconductor nanoparticles coupled with TiO$_2$ is probably not due to the photocatalytic properties of the ferric semiconductors, but rather an extended photoresponse of a delicately-prepared coupled system with charge or transfer phenomena that has been currently unexplained although proven experimentally. Additional research is needed to explore and determine the extended photoresponse of coupled semiconductor nanoparticles where photosensitization is not the suggested cause of photocatalysis.
CHAPTER 4
EXPERIMENTAL APPROACH

4.1 Investigation of Nanoparticle Coupling

Of the various possible methods discussed to potentially design and create visible light photocatalysts, the study of nanoparticle coupling was chosen because of its optimistic although uncertain potential and low-cost chemical preparation methods. It is an area of earnest interest because of the unusually limited experimental and theoretical explanations provided even for common photocatalysts such as TiO$_2$. In fact, only a relatively limited number of research papers have been published on TiO$_2$ alloys used for visible light photocatalysis, excluding the more common TiO$_2$-CdS synthesized alloys. Theoretical explanations have been almost completely avoided for coupled systems where photosensitization mechanisms are not an immediate explanation. Despite the lack of existing research and theoretical explanations, current experimental results suggest an unparalleled optimism over other methods of visible light photocatalysis, since it offers a photoresponse extended beyond that of chemically ion-implanted and non-metal doping techniques while avoiding toxicity concerns related to current photosensitization systems. It is clear that further research on the coupling of semiconductor nanoparticles is necessary to clarify and identify this potential phenomenon for visible light photocatalysis.
As mentioned in section 3.2.3, over a dozen metal oxide and metal sulfide semiconductors have been coupled with TiO$_2$ for a wide range of applications. A significantly reduced amount of studies, however, have been conducted on semiconductor coupling for the purpose of photocatalysis. For the photocatalytic enhancement of TiO$_2$ under UV irradiation, WO$_3$ has been the most commonly studied catalyst for coupling because of its ability to decrease the EHP recombination of TiO$_2$ through photosensitization mechanisms, as well as its ability to inhibit the anatase-to-rutile transformation [58-60]. For the extension of the photoresponse of coupled TiO$_2$ nanoparticles to visible wavelengths, few semiconductors have been studied. The photocatalyst CdS, as has already been discussed, has drawn the most attention but is considered unlikely as a practical candidate due to its toxicity. The nontoxic semiconductor photocatalyst ZnFe$_2$O$_4$ has been suggested for coupling due to its ability to absorb visible light using its narrow 1.9eV band gap, while reportedly not being susceptible to photoanodic corrosion. A study on the synthesis, characterization, and photocatalytic activity of TiO$_2$-ZnFe$_2$O$_4$ coupled nanocomposites has been conducted using a multi-stage synthesis approach [61]. Positive results of the photocatalytic activity of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites for the photodegradation of phenol under solar irradiation have been reported. It was not determined, however, if the increased photocatalytic activity was due to an extended photoresponse suggesting visible light photocatalysis, or if it was due to a charge separation effect increasing the UV photoactivity of TiO$_2$ through EHP recombination.

This research investigates TiO$_2$-ZnFe$_2$O$_4$ coupled nanocomposites as a potential nontoxic visible light activated photocatalyst. Furthermore, TiO$_2$ doped with small mole...
percents of Zn\(^{2+}\) and Fe\(^{3+}\) ions has been investigated for comparison of doped and alloyed composites. Determinations will be made as to photocatalytic performances under UV, visible, and solar simulated irradiation conditions to attempt and classify charge transfer reaction mechanisms or other structural parameters affecting photocatalysis.

4.2 Photocatalyst Preparation Procedures

Two separate chemical procedures were used throughout this study to compare the alloying of TiO\(_2\) with merely doping. A two-step coprecipitation / hydrolysis technique was used to create TiO\(_2\)-ZnFe\(_2\)O\(_4\) alloys, and a sol-gel technique was used for creating TiO\(_2\) doped with Zn\(^{2+}\) and Fe\(^{3+}\) ions. All catalysts were chemically optimized and evaluated for photoactivity, crystal structure, particle size, as well as other characteristics, in order to determine the photocatalytic effectiveness of Zn and Fe incorporated TiO\(_2\).

4.2.1 TiO\(_2\)-ZnFe\(_2\)O\(_4\) Alloys

The n-type semiconductor TiO\(_2\) has been prepared in a myriad of preparation procedures including precipitation, sol-gel, impregnation, flame synthesis, controlled hydrolysis, spray pyrolysis and r.f. sputtering among others [5]. Factors affecting the structure and properties of chemically-prepared TiO\(_2\) can be described as composition related (such as the chosen titanium precursor) or described as procedural (such as the pH range) which is particularly important for this project. When TiO\(_2\) is created using chemical synthesis methods, acidic conditions are usually favored and are occasionally mandatory, as in sol-gel procedures; however, this is not always the case, and reports
have confirmed that benefits can be achieved from TiO$_2$ prepared using both acidic and alkaline preparation conditions. For example, it has been suggested that TiO$_2$ prepared under acidic conditions can promote the anatase-to-rutile transformation at low temperatures, and TiO$_2$ prepared under alkaline conditions can retard the transformation as well as prevent particles from aggregating [62].

Zinc ferrite (ZnFe$_2$O$_4$) is an n-type semiconductor characterized by a spinel structure with a tetrahedral A site by Zn$^{2+}$ ions and an octahedral B site by Fe$^{3+}$ ions [63]. ZnFe$_2$O$_4$ is most prominently known for its magnetic properties; however, its electrical, gas sensing and catalytic characteristics have also been studied. In contrast to TiO$_2$, ZnFe$_2$O$_4$ is usually and perhaps most facilely prepared using chemical coprecipitation procedures performed under alkaline conditions followed by calcination temperatures ranging from 600-900°C [64, 65], although several recent reports have suggested synthesis through sol-gel procedures [66, 67] and mechanochemical methods by the mechanical alloying (MA) of ZnO and Fe$_2$O$_3$ [68]. As a low band gap (1.9eV) semiconductor, ZnFe$_2$O$_4$ has attracted attention as a potential photocatalyst due to its ability to absorb visible light of wavelengths less than 652nm. ZnFe$_2$O$_4$ does face its share of problems, including an energetically unfavorable conduction band and surface adsorption characteristics.

The fundamental difficulty in creating TiO$_2$-ZnFe$_2$O$_4$ nanocomposites relates to their incompatibilities in preparation procedure. As discussed, the photoactive anatase phase of TiO$_2$ is usually prepared under acidic conditions followed by low temperature calcination procedures (400-600°C, depending on preparation procedure), and ZnFe$_2$O$_4$ is usually prepared under alkaline conditions followed by high calcination temperatures to
enhance crystallinity (600-900°C). To the best of the author’s knowledge, only one paper has been published on TiO$_2$-ZnFe$_2$O$_4$ alloys, although there have been several recent reports, most occurring in the past year, regarding the doping of TiO$_2$ using ZnFe$_2$O$_4$ or co-doping using Zn$^{2+}$ and Fe$^{3+}$ ions. A reported TiO$_2$-ZnFe$_2$O$_4$ nanocomposite alloy was created in 2001, using separate hydrolysis and coprecipitation techniques for TiO$_2$ and ZnFe$_2$O$_4$, respectively, followed by surfactant capping to create an organic sol consisting of the desired alloy that could be fired and dried to form a powder [61]. This relatively complex technique suggested promising results for photocatalytic degradation of phenol under solar illumination; however, a more direct and manageable synthesis route was desirable, and a clarification was needed as to whether the photocatalytic activity was enhanced in the UV range of the solar spectrum or if the photoresponse of the catalyst was extended to visible wavelengths.

It was desirable that a simple and consistent synthesis route be discovered for the formation of a TiO$_2$-ZnFe$_2$O$_4$ nanocomposite with alloying molar ratios of TiO$_2$:ZnFe$_2$O$_4$ as high as 1:0.2. The photocatalytic activity of the alloys could then be identified and conclusions could be drawn as to whether the alloying of TiO$_2$ with the visible light responsive photocatalyst ZnFe$_2$O$_4$, increased the photoactivity of TiO$_2$ under UV irradiation through charge separation methods, extended the photoresponse to the visible range through some type of charge transfer mechanism, or had an overall negative impact on the photocatalytic efficiency of TiO$_2$.

As outlined in Figure 4.1, a sensitive two-step coprecipitation / hydrolysis method was created for the purpose of synthesizing TiO$_2$-ZnFe$_2$O$_4$ alloys.
All chemicals used were provided by Sigma Aldrich and were characterized by 99.9% purity or higher. 1-Propanol (C₃H₇OH) was chosen as a solvent instead of ethyl alcohol due to its higher boiling point of 97°C, since heating in the ranges of 60-75°C would be involved in preparation procedures. H₂O could not be used as a solvent, since an
immediate and undesirable hydrolysis reaction would occur when the titanium precursor is later added. ZnFe$_2$O$_4$ was created by coprecipitating the respective nitrate precursors Fe(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O under vigorous stirring and heating at 65°C. A 3.5M NH$_4$OH solution using C$_3$H$_7$OH as a solvent was used not only to increase the pH above at least 4, which was needed to coprecipitate ZnFe$_2$O$_4$ under the given conditions, but also to add small amounts of H$_2$O to the solution, since NH$_4$OH contains approximately 70wt% H$_2$O. The molar concentration of NH$_4$OH was carefully chosen so that the maximum pH (preferred by ZnFe$_2$O$_4$) could be attained without aggregating the particles or causing immediate coprecipitation. Titanium(IV) butoxide, Ti[O(CH$_2$)$_3$CH$_3$]$_4$, or (Ti[OBu]$_4$), was chosen as the titanium precursor since it is inexpensive and able to hydrolyze using small amounts of H$_2$O per ratio of Ti, which was important since small amounts of H$_2$O would be used. The TiO$_2$ was subtly hydrolyzed in the homogeneous neutral pH coprecipitated solution using the H$_2$O from the NH$_4$OH solution and the H$_2$O from the previous step. To prevent immediate hydrolysis, the Ti(OBu)$_4$ and C$_3$H$_7$OH (anhydrous) were respectively mixed in a 1:2wt% ratio and then the resulting solution was added dropwise to the parent solution. The solution was kept stirring at 65°C for 90 minutes, followed by filtering and drying at 100°C for 6 hours. The powder was then ground with a mortar and pestle and heated in a static air atmosphere slowly to 220°C to heat the powder past the exothermic reaction caused by the burning off of the nitrates. Calcination under flowing air atmosphere at temperatures between 400-600°C was performed by placing the nanoparticles in a ceramic boat contained in a hollow high temperature glass tube and heated using a Thermolyne tube.
furnace. The calcination configuration was chosen after several attempts with stainless steel and glass apparatuses proved to provide low crystallinity.

4.2.2 TiO$_2$ Doped with Fe$^{3+}$ and Zn$^{2+}$ Ions

Since the first publication in 2000, only a few papers have been published on either the co-doping of TiO$_2$ with Fe$^{3+}$ and Zn$^{2+}$ or by ZnFe$_2$O$_4$ in concentrations of approximately 2wt% or less, although the recent trend in the past years shows an increased interest. The first two publications used r.f. magnetron sputtering to create doped thin films for phase identification and photoluminescence studies [69, 70], and more recent publications in the past year have used sol-gel techniques to study photocatalysis [71, 72, 73]. The theoretical objective reported in all of the dopant studies is to extend the photoresponse of TiO$_2$ through doping of a visible light activated photocatalyst ZnFe$_2$O$_4$, in contrast to enhancing the performance of TiO$_2$ through preventing charge carrier recombination. It should be noted that slight traces of ZnFe$_2$O$_4$ was confirmed by XRD studies for r.f. sputtering techniques, although no such peaks were observed for sol-gel procedures. Although it is probable that the XRD is unable to effectively determine the small dopant concentrations, it is also likely that ZnFe$_2$O$_4$ is difficult to form through sol-gel methods primarily because of the room temperature acidic preparation conditions and rather Fe$^{3+}$ and Zn$^{2+}$ ions are incorporated into the TiO$_2$ surface structure.

A thorough study of the photocatalytic activity of sol-gel prepared TiO$_2$ doped with Fe$^{3+}$ and Zn$^{2+}$ ions was desired for two reasons. First and foremost, recent photocatalytic studies on this topic have suggested an increase in solar irradiated organic
degradation reactions, although determinations have not been made as to whether this is caused by Fe\(^{3+}\) and Zn\(^{2+}\) ions or ZnFe\(_2\)O\(_4\) acting as traps in the surface of the TiO\(_2\) lattice, or if it is a slight extension of the photoresponse to visible wavelengths. Secondly, a determination needs to be made as to whether ZnFe\(_2\)O\(_4\) can actually be created using sol-gel procedural conditions, or if it truly is merely ion doping from the Fe and Zn precursors.

Sol-gel procedures have been used regularly since the 1950s to obtain particles with higher purity and homogeneity at lower processing temperatures than available by many other traditional methods. As outlined in Figure 4.2, an adopted sol-gel technique was used and modified for the controlled hydrolysis of a Ti alkoxide co-doped with Fe\(^{3+}\) and Zn\(^{2+}\) ions [45] using an plenary molar ratio of Ti(OBu)\(_4\) : C\(_2\)H\(_5\)OH : H\(_2\)O : HNO\(_3\) equivalent to 1 : 20 : 6 : 0.8-0.45. 13.5 moles of anhydrous ethanol (C\(_2\)H\(_5\)OH) was first mixed with 1 mole of Ti(OBu)\(_4\) and stirred for ten minutes at room temperature. When creating pure TiO\(_2\), 0.8 moles of HNO\(_3\) was added dropwise to the solution to stabilize the Ti precursor so that immediate hydrolysis would not occur upon the following addition of H\(_2\)O. When doped TiO\(_2\) was created, less HNO\(_3\) was used to compensate for the added acidity contributed by the Fe and Zn nitrate precursors, in efforts retain the same gelling rate for all samples. A separate solution of 6.5 moles of C\(_2\)H\(_5\)OH and 1 mole of deionized H\(_2\)O was vigorously stirred and added dropwise to the parent solution when pure TiO\(_2\) was created. For doped TiO\(_2\), Fe(NO\(_3\))\(_3\) \cdot 9H\(_2\)O and Zn(Fe\(_3\))\(_2\) \cdot 6H\(_2\)O were added to this solution in a Fe:Zn molar ratio of 2:1, as if ZnFe\(_2\)O\(_4\) would be the resulting formation.
The final pH of doped and un-doped solutions was 0.85, which allowed for gelation times of approximately 12 hours for all samples. If the pH was lowered to 0.70, gelation would not occur and if the pH was raised to 1.0, an immediate and undesirable gelation would take place. The concentration of HNO₃ was therefore a critical step in this process, especially when the Fe and Zn nitrates were included. The resultant
dispersion of colloidal particles defined as the sol, was aged and allowed to gel at room
temperature for 48 hours, followed by heating at 85°C for solvent removal. The
remaining particles were slowly heated up to 145°C to avoid calcination during the
exothermic reaction caused by the Ti(OBu)₄ precursor. The resulting powders were
calcined in a flowing air atmosphere identical to that of the alloy nanocomposites.

4.3 Determination of Photocatalytic Activity

Various methods have been proposed in literature to test and compare the
photoactivity of both powder and thin-film semiconductor photocatalysts. The most
conventional method is the degradation of an organic compound using an irradiated
reactor containing the desired catalyst, degradant, and electron scavenger. The most
commonly used test degradants reported in literature for the testing of TiO₂ have been
phenolic compounds or dyes such as methylene blue and methyl orange.

Phenol was chosen for several reasons as a test degradant for all photoactivity
experiments in this study. The primary reason is that phenol is an ideal degradant for
visible light photocatalysis measurements because it absorbs only UV-C irradiation with
an absorption peak between 265 and 270nm, implying that it will not be susceptible to
photolysis when irradiated by UV-A and visible light. In contrast, dyes such as
methylene blue and methyl orange will experience degradation due to photolysis promoted
by visible irradiation. Phenol is also a test degradant that exhibits application, since it is a
common contaminant of industrial effluents. Photocatalytic oxidation of phenolic
compounds in industry has been suggested to replace other processes such as activated
carbon adsorption, chemical oxidation, biological treatment, wet oxidation, and
The photocatalytic activity testing of the fabricated catalysts was the focal point of this study and thus several reactors were created to thoroughly test the catalysts under UV-A, visible, and a combination of UV-A and visible irradiation as a simulation of natural sunlight. In all reactor configurations, a 1000mL borosilicate photochemical reaction vessel was used to contain the reaction and a borosilicate immersion well was incorporated for irradiation purposes. Deionized water was used to suspend the aqueous slurry containing phenol and the catalyst under test, and air was injected at a rate controlled by a rotameter for the purpose of scavenging electrons photogenerated in the reaction.

Photocatalytic experiments using UV-A irradiation were performed using an annular reactor with a centralized reaction vessel as shown in Figure 4.3. The irradiation was provided by four UV-A lamps penetrating the perimeter of the reaction vessel and one UV-A lamp irradiating isotropically from inside the immersion well. The
approximate irradiance on the surface of the reaction vessel was $90\text{W/m}^2$ with a center wavelength of 368nm and a FWHM of 19nm.

![Diagram of UV Photocatalytic Reactor](image)

Figure 4.3   UV Photocatalytic Reactor Used for TiO$_2$ Degradation Studies.

As shown in Figure 4.4, photocatalytic experiments using visible light and a combination of UV-A and visible light were performed using a single lamp and an annular reflector to provide irradiation to all sides of the reaction vessel. The immersion well was used as a means of concentrating the aqueous solution to the perimeter of the reaction vessel to optically optimize the system. A 1000W metal halide lamp was experimentally chosen, since it adequately replicated both the pattern and intensity peaks of the solar spectrum more accurately than other visible sources such as high pressure
sodium and fluorescent lamps. The metal halide spectrum, as shown in Figure 4.5 and Figure 4.6, was found to contain sufficient UV-A radiation in the range of 350-400nm to serve as both a UV-A and visible light source. For photocatalytic experiments using purely visible light, a longpass UV filter provided by Edmund Optics was used to cut off the wavelengths shorter than 400nm, at a cost of approximately 8% attenuation at wavelengths greater than 400 nm. The system was cooled from 110°C to 70°C using ventilation provided by three fans inputting and removing air from the surface of the lamp and inside the reactor.

Figure 4.4 UV Vis / Visible Light Photocatalytic Reactor Used for TiO₂ Degradation Studies.
Figure 4.5 UV-Vis Metal Halide Spectrum Compared to Solar Irradiation.

Figure 4.6 Effects of UV-cutoff Filter on Metal Halide Irradiation Pattern.
Photocatalytic phenol degradation experiments were conducted using the following universal procedures regardless of the photoreactor used for testing. A solution of deionized water, phenol, and the catalyst under test were mixed using magnetic stirring, and air was injected to scavenge photogenerated electrons and also to help suspend the catalyst. The phenol concentration in all experiments was 40ppm which was selected as a value large enough to accurately measure using absorption measurements and small enough to degrade within hours when exposed to an efficient photocatalyst. Air was dispersed in the aqueous solution through a 12-inch rod sparger and was used in place of pure O$_2$ to simulate real-world experimental conditions. Periodic 1.5mL samples were retrieved from the reaction vessel in desired time increments and placed in Eppendorf microcentrifuge tubes for analysis of the photocatalytic degradation of phenol. The nanoparticle catalysts were separated from the phenol and water mixtures by centrifuging the Eppendorf tubes for 10 minutes at 4000rpm and 3220rcf using an Eppendorf 5810R centrifuge. UV-Vis spectroscopy using an Ocean Optics USB2000 fiber optic spectrometer was used to analyze the degradation of phenol with respect to time by monitoring the intensity of the absorption peak of phenol located at 268.63nm. Phenol degradation was determined with respect to its initial concentration, and therefore all degradation plots are normalized based on $C/C_0$ values which are interpreted as the concentration at the measured time divided by the initial concentration. Although 40ppm of phenol was carefully maintained for initial phenol concentrations, spectroscopy results displayed up to 7% differences in initial intensities of phenol absorption peaks. To compensate for any error, the initial phenol peaks were normalized to ensure accurate and comparable degradation rates. The provided procedure and the accuracy of the
spectrometer resulted in error margins of approximately 2% (C/C₀) or less for all phenol degradation measurements.

### 4.3.2 Control Conditions and Experiments

Experimental conditions that directly affect the degradation of phenol through photocatalytic oxidation processes include the initial concentration of the pollutants, light intensity, initial pH of the solution, rate of circulating air flow, amount of O₂ for electron scavenging, and catalyst loading concentration. All of these parameters were either controlled or experimentally optimized and standardized so that careful comparisons can be made on sensitive catalyst design comparisons.

The light intensity for all three reactor configurations was nonadjustable and therefore only varied by naturally degrading over time. The recommended lifetime of the UV-A lamps and the metal halide lamp was 3000hrs and 8000hrs respectively, so although the lamps were used for less than approximately 10% of their recommended lifetimes, precautions on degradation of light intensity were taken by only comparing photocatalytic measurements performed within a credible time frame.

The initial pH of the aqueous solution affects the catalytic properties of TiO₂, since according to the zero-point charge of TiO₂, its surface is positively charged in acidic media and negatively charged in acidic media [74]. More hydroxyl radicals can be induced in acidic media since there is a higher concentration of H⁺ ions; therefore, the photocatalytic oxidation of phenol is usually found to increase with decreasing pH. This factor was suppressed in all experiments by using a fixed concentration of phenol providing a natural pH of 6.5, although it should be noted that the pH of the aqueous
solution decreases with time due to the formation of HCl during the degradation process [75].

The flow rate of air injected into the photoreactor was controlled by a rotameter and varied between 0-2.5L/min to find an optimal standard for all succeeding experiments. O₂ dissolved in the solution is used to scavenge photogenerated electrons; therefore, the amount of air needed is not only a function of the reactor design but also of the photocatalytic performance of an individual catalyst and its ability to create EHP that can migrate to the surface of the photocatalytic particle. Since the optical and electrical characteristics vary depending on the catalyst used, an optimal air flow rate can only be determined for general conditions. Control tests were conducted (as shown in Figure 3) using the UV-A / Vis reactor to find the optimal air flow rate using pure anatase TiO₂ provided by Aldrich using a catalyst loading of 0.5g/L. It should be noted that the photocatalytic performance increased with increasing air flow rate until about 1.5L/min where it stabilized and began to decline after 2.0 L/min. An air flow rate of 1.5L/min was used for the remainder of experiments.
The effects of catalyst loading were also studied using Aldrich’s TiO$_2$ as a photocatalyst using the UV-A / Vis reactor. The phenol degradation rate depends primarily on the number of active sites on the photocatalyst’s surface. The optimal catalyst loading will therefore be a trade-off of the maximum catalyst concentration with the maximum light penetration into the aqueous solution. These two variables are inversely proportional and therefore a wide range of catalyst loadings will provide similar phenol degradation rates as shown in Figure 4. This is beneficial since it allows an important degree of freedom in the reaction. For instance, the loading of a catalyst for a photocatalytic reaction in an aqueous solution is actually a function of surface area and not solely the mass or volume quantities that are commonly used to determine catalyst concentrations. Based on the results from this experiment, it was determined that a minimal catalyst loading of 0.5g/L should be used for photocatalysts characterized by a
large surface area, and increased loading should be used as appropriate for catalysts characterized by low surface areas. From Figure 4, it should also be noted that phenol is not susceptible to photolysis under UV-A or visible light as previously stated.

Figure 4.8 Photocatalytic Degradation Control Experiment for Catalyst Loading.
CHAPTER 5
EXPERIMENTAL RESULTS

5.1 TiO$_2$-ZnFe$_2$O$_4$ Alloys

As discussed in Section 4.2, a straightforward, repeatable, and inexpensive chemical procedure was sought for the synthesis of TiO$_2$-ZnFe$_2$O$_4$ alloys for the investigation of visible light photocatalysis. The primary theoretical objectives were to create TiO$_2$-(X)ZnFe$_2$O$_4$ alloys, where X can range between 0.01 and 0.2 moles. In attempts to maximize photocatalytic activity, it was desired to obtain TiO$_2$ with the maximum anatase-to-rutile ratio and the highest possible surface area. Assuming that an extension in the photoresponse to longer wavelengths would be attributed to interfacial charge transfer, it was also desired to create ZnFe$_2$O$_4$ nanoparticles of sizes relative to or smaller than the contiguous TiO$_2$ particles. Although the catalyst may not necessarily be photoactive over its entire absorption region, it was also desired to shift the absorption edge to longer wavelengths to maximize the possibilities of photon to EHP to charge transfer reactions.

5.1.1 Coprecipitated ZnFe$_2$O$_4$

Pure ZnFe$_2$O$_4$ was first investigated to determine which of its structural properties could be manipulated during chemical synthesis methods. A critical initial step in
creating TiO$_2$-ZnFe$_2$O$_4$ alloys was to ensure that ZnFe$_2$O$_4$ could form under the limited preparation conditions imposed by the alloying process. For this first analysis, ZnFe$_2$O$_4$ was created using a simple one-step coprecipitation method, since its chemical synthesis had possibilities of correlating with the hydrolysis reaction of TiO$_2$. The coprecipitation of two or more metallic compounds often provides poor homogeneity because the composition of the precipitate depends on the differences in the solubility between the components and the chemistry occurring during precipitation [24]. For this reason, it was desirable to use highly soluble precursors for the formation of an amorphous compound that could be decomposed and crystallized under mild calcination temperatures. Figure 4.1 outlines the coprecipitation ZnFe$_2$O$_4$ using the respective highly soluble nitrate precursors Fe(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O, where the product is essentially formed by an energetically favorable combination of a wide band gap (ZnO) and narrow band gap (Fe$_2$O$_3$) semiconductor.

\[
\text{ZnO} + \text{Fe}_2\text{O}_3 \rightarrow \text{ZnFe}_2\text{O}_4 \tag{12}
\]
Figure 5.1 Coprecipitation Procedure for the Formation of ZnFe$_2$O$_4$.

The molar ratio of the primary solution consisting of C$_3$H$_7$OH : Fe : Zn was equivalent to 100 : 2 : 1, with a C$_3$H$_7$OH mass of 163g. Isopropanol was chosen as the solvent instead of H$_2$O to simulate the synthesis conditions that ZnFe$_2$O$_4$ will undergo when TiO$_2$ is later incorporated. The solution was vigorously stirred for 45 minutes while heated at 65°C, which is above the boiling point of each nitrate precursor. A 3.5M NH$_4$OH solution was added dropwise to the parent solution until the desired pH was reached and measured by a calibrated Oakton pH meter. The pH must be raised above approximately 4 to precipitate the nitrate precursors. A 3.5M NH$_4$OH solution was
chosen to provide a maximum (of approximately 7), while low enough in concentration to avoid undesirable precipitation at the solution’s surface upon impact. After stirring, the solution was immediately filtered and dried in a static air atmosphere at 100°C for 6 hours to evaporate the C\textsubscript{3}H\textsubscript{7}OH followed by a slow heating to 225°C to exceed the temperatures of intense exothermic reactions caused by the thermal decomposition of the nitrate precursors. Calcination was performed using the same procedure described in Section 4.2.

Governable parameters that are critical for the coprecipitation of ZnFe\textsubscript{2}O\textsubscript{4} were determined primarily to be the pH of the solution and the final calcination temperature. Although both parameters have been suggested to affect the crystallinity and particle size of the sample, these factors widely vary depending on preparation procedure and therefore must be analyzed using the current procedure. To represent the possible preparation conditions for TiO\textsubscript{2}-ZnFe\textsubscript{2}O\textsubscript{4} alloys, ZnFe\textsubscript{2}O\textsubscript{4} was coprecipitated using pHs of 5, 6, and 7 and calcined at 500°C. XRD analysis of the two dominant ZnFe\textsubscript{2}O\textsubscript{4} peaks (Figure 5.2) revealed that the pH condition of the coprecipitated solutions over the range studied, did not significantly affect the particle’s crystallinity, allowing a flexible region in the nanocomposites preparation procedure. XRD analysis was also performed to analyze the affect of calcination temperature on the crystallinity of ZnFe\textsubscript{2}O\textsubscript{4}. Figure 5.3 shows the critical nature of annealing on ZnFe\textsubscript{2}O\textsubscript{4}’s crystallization as the crystallinity rapidly increases with temperature and the particle size subsequently decreases. The calcination temperature of the nanocomposite will therefore be consequential to the particle size and crystallinity of the ZnFe\textsubscript{2}O\textsubscript{4} particles.
Figure 5.2  XRD Spectra Displaying the Effect of pH on the Crystallinity of Coprecipitated ZnFe$_2$O$_4$.

Figure 5.3  XRD Spectra Displaying the Effect of Calcination Temperature on the Crystallinity of Coprecipitated ZnFe$_2$O$_4$. 
The photocatalytic degradation of ZnFe$_2$O$_4$ was analyzed using two separate photoreactors for UV and visible light phenol degradation studies. As discussed in Section 4.3, the UV and visible light reactors use different irradiation sources and therefore the degradation rates shown in Figure 5.X should not be directly compared due to differences in photon fluxes. ZnFe$_2$O$_4$ was prepared by coprecipitation in a solution with a pH equal to 6 and calcined at a moderate temperature of 450°C (to coincide with later studies). It was determined from Figure 5.4 that ZnFe$_2$O$_4$ is photocatalytic under the narrow band UV-A irradiation and also under visible light irradiation with wavelengths between 400 and (presumably as high as) 652nm. In contrast to the photodegradation curves of TiO$_2$, the photoactivity of ZnFe$_2$O$_4$ ceases after a short duration. This phenomenon has been attributed to the ZnFe$_2$O$_4$’s adsorption of intermediate oxidation by-products such as hydroquinone, catechol, and benzoquinone, which competitively inhibit the adsorption of phenol [77]. Although this is an unfavorable characteristic of ZnFe$_2$O$_4$, disabling an otherwise visible light activated photocatalyst will allow for later conclusions to be made regarding the role of ZnFe$_2$O$_4$ in a TiO$_2$-ZnFe$_2$O$_4$ nanocomposite.
5.1.2 Hydrolyzed TiO₂

As previously discussed in Section 4.2, TiO₂ can be formed by a wide variety of synthesis methods. In attempts to create TiO₂–ZnFe₂O₄ alloys, however, preparation procedures are unduly limited and have thus far reportedly been confined to meticulous multi-step colloidal chemistry methods and perhaps the more obvious, yet unreported, (although possibly photocatalytically ineffective) mechanochemical processing of amorphous composites. It was decided that the most proficient method of synthesizing TiO₂ with coprecipitated amorphous ZnFe₂O₄ was through controlled hydrolysis, since this can be performed in a wide range of pH conditions utilizing the H₂O found in the coprecipitated solution.
The hydrolysis of alkoxides consists of two general stages: a hydrolysis stage and a condensation stage. In the hydrolysis stage, the titanium alkoxide precursor will hydrolyze upon contact with H₂O molecules to form Ti-OH bonds. This hydrolysis reaction should be near completion before the condensation reaction occurs. During the condensation stage (which should slowly occur), Ti-O-Ti bonds form, resulting in 3-dimensional structure that eventually precipitates from the solution. Titanium(IV) butoxide, Ti[O(CH₂)₃CH₃]₄, was chosen as the Ti precursor and can be readily hydrolyzed to form TiO₂ and butyl alcohol (and possibly a small variety of co-products) following the following reaction pathway:

\[ \text{Ti}[O(CH₂)₃CH₃]₄ + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{C}_₄\text{H}_₉\text{OH} \] (13)

The equivalent hydrolysis method for creating pure TiO₂ from the TiO₂-ZnFe₂O₄ alloyed synthesis technique used in this study is shown in Figure 5.5, where the addition of the Zn and Fe nitrate precursors were excluded, maintaining only the role coinciding with the synthesis of TiO₂. The purpose of this experiment was not to create photocatalytically or structurally optimized TiO₂ nanoparticles, but rather to analyze and characterize the hydrolyzed TiO₂ that will be formed in the TiO₂-ZnFe₂O₄ alloy.

Anhydrous C₃H₇OH was mixed with deionized 29.11g of H₂O using a respective molar ratio of 1:0.8. After vigorous stirring, a second solution of C₃H₇OH and 11g of Ti[O(CH₂)₃CH₃]₄ combined in a 1:0.077 molar ratio were slowly added to the parent solution for a deliberate hydrolysis reaction. After 90 minutes of stirring, the sample was immediately filtered, dried, and calcined at a modest temperature of 450°C to avoid any rutile phase formation.
It should be noted that, although the hydrolysis of a titanium alkoxide precursor may work well for the integration of ZnFe₂O₄ prepared by coprecipitation techniques, it is not normally considered an optimal synthesis route when concerns exist with regard to superlative crystallization, controllability of particle size, or photocatalytic activity. For purposes of providing a general comparison, Figure 5.X shows an XRD plot of the highly crystalline, pure anatase Aldrich TiO₂ (advertised average particle size of 25-70nm) compared with TiO₂ nanoparticles (average particle size of 22.5nm) prepared by the conventional hydrolysis technique of an alkoxide precursor as shown in Figure 5.5. Figure 5.7 compares the photocatalytic activity of the highly crystalline Aldrich TiO₂
with the same TiO$_2$ prepared from a general hydrolysis technique when the samples are irradiated using the UV-A photoreactor. Aldrich TiO$_2$ was chosen as an *ideal* commercially available photocatalyst for comparison with the hydrolyzed sample, since its degradation of phenol under the designated test conditions was found to be superior even to the commonly used Degussa P-25 reference catalyst. The superior photocatalytic activity of the Aldrich TiO$_2$ is evident by its 79.2% degradation compared to that of the 32.2% degradation provided by the hydrolyzed TiO$_2$.

![Graph showing comparison of crystallinity between Aldrich TiO$_2$ and TiO$_2$ prepared by a general hydrolysis procedure.](image)

**Figure 5.6** Comparison of Crystallinity between Aldrich TiO$_2$ and TiO$_2$ Prepared by a General Hydrolysis Procedure.
Although visible light (>400nm) photocatalytic reactions carried out by TiO$_2$-ZnFe$_2$O$_4$ nanocomposites are not theorized to be primarily related to redox reactions occurring on the surface of the large band gap TiO$_2$ particles, it was still desired to optimize the TiO$_2$ for purposes such as solar irradiated photoreactions as well as any unforeseen charge transfer mechanisms. Various methods of enhancing the photoactivity of hydrolyzed TiO$_2$ have been suggested in literature, including the use of various precursors such as TiCl$_4$, hydrothermal treatments, multi-stage pH control techniques, and particle size tailoring [62, 78-80].

In efforts to enhance or at the very least determine the influences affecting the established hydrolysis technique while retaining the same Ti(OBu)$_4$ precursor, studies on the effects of pH and H$_2$O:Ti(OBu)$_4$ ratio were conducted. Amorphous TiO$_2$ was
hydrolyzed in aqueous solutions characterized by a pH range of 3-9. The pH of the naturally neutral solution as prepared in Figure 5.5 was lowered using several drops of a 0.75M HNO$_3$ solution, and raised using several drops of a 1M NH$_4$OH solution. Phenol degradation experiments performed by irradiating the hydrolyzed samples with UV-A irradiation show that the photocatalyst’s activity increases with decreasing pH over the pH range of 3-9 (as shown in Figure 5.6). This is thought to be attributed to the fact that acidic conditions enhance the rate of the hydrolysis reaction and decreases the rate of condensation. Although preparation solutions with lower pHs appear favorable for the purpose of creating hydrolyzed catalysts with optimum photocatalytic activity, a pH of at least 4 must be used when a TiO$_2$-ZnFe$_2$O$_4$ nanocomposite is created in order to properly coprecipitate the Fe and Zn nitrate precursors.

![Figure 5.8](image-url)  
**Figure 5.8**  UV Activated Photocatalytic Degradation Rates for Hydrolyzed TiO$_2$ Prepared in Solutions of Various pHs.
The Ti precursor to water ratio for hydrolysis reactions, commonly referred to as \( h = \frac{[\text{H}_2\text{O}]}{[\text{Ti}(	ext{OBu})_4]} \), has been determined to influence parameters such as particle size and the induction time required for the initiation of the hydrolysis reaction [81]. Using the hydrolysis procedure outlined in Figure 5.5, the effect of \( \text{H}_2\text{O} \) concentration on the particle size and UV-A irradiated photocatalytic activity were determined for ratios of \( h = 5, 15, 25, \) and \( 50 \), using a pH of 5. The increasing concentrations of both the \( \text{H}_2\text{O}:\text{Ti}(	ext{OBu})_4 \) and \( \text{Ti}(	ext{OBu})_4: \text{C}_3\text{H}_7\text{OH} \) ratios were found to increase the rate of solid phase formation. It was determined that \( \text{TiO}_2 \) hydrolyzed with \( h \) values lower than approximately 25 would be incapable of sufficient hydrolysis due to the inadequate concentration of \( \text{H}_2\text{O} \) molecules and using \( h \) values higher than 50 would not practically correlate with the synthesis of \( \text{ZnFe}_2\text{O}_4 \) in later experiments. As shown in Figure 5.9, XRD measurements showed pure anatase phases of uniform crystallinity and particle size among all four samples.

Despite the uniformity of structural characteristics, hydrolyzed \( \text{TiO}_2 \) prepared with different \( h \) values proved to have photocatalytic activity that increased with the value of \( h \), as shown in Figure 5.10. This relationship could possibly be attributed to several factors, including the partial hydrolysis of \( \text{TiO}_2 \) prepared with low \( h \) ratios and therefore corresponding to longer induction times. Another factor could be the slight difference in the mean particle size, which was determined to be 25.2, 23.6, 20.3, and 19.5nm for respective \( h \) values of 5, 15, 25, and 50.
Figure 5.9  XRD Spectra of Hydrolyzed TiO$_2$ with $h = [\text{H}_2\text{O}] / [\text{Ti(Obu)}_4]$ (all lattice planes correspond to anatase crystal structure).

Figure 5.10  UV Activated Photocatalytic Degradation Rates for Hydrolyzed TiO$_2$ with $h = [\text{H}_2\text{O}] / [\text{Ti(Obu)}_4]$. 

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5.1.3 Preparation of TiO$_2$-ZnFe$_2$O$_4$ Alloys

The ideal TiO$_2$-ZnFe$_2$O$_4$ nanocomposites are thought to be a two-phase structure that will allow sufficient photons to be absorbed by the low band gap ZnFe$_2$O$_4$ particles, while maintaining an intimate particle interaction to provide diffusion pathways for charge carriers. Several conclusions can be drawn from experiments conducted on the preparation and analysis of individually coprecipitated ZnFe$_2$O$_4$ and hydrolyzed TiO$_2$ particles. Experiments outlined in Section 5.1.1 suggested that highly crystalline ZnFe$_2$O$_4$ could be prepared at under low temperatures using a simple coprecipitation procedure. Experiments conducted in Section 5.1.2, suggested that when using the selected hydrolysis synthesis conditions for pure TiO$_2$, the photocatalytic activity of the crystalline nanoparticles can be optimized by decreasing the pH of the parent solution and by increasing the [H$_2$O]:[Ti(OBu)$_4$] ratio.

The contrasting results from Sections 5.1.1 and 5.1.2 outline the difficulty in creating photocatalytically optimized TiO$_2$-ZnFe$_2$O$_4$ nanocomposites. The first step in characterizing these alloys was to verify the successful creation of a two-phase nanocomposite using the provided coprecipitation / hydrolysis synthesis method. This was accomplished by verifying the spinel ZnFe$_2$O$_4$ crystal structure using XRD analysis on a sample with a high TiO$_2$:ZnFe$_2$O$_4$ molar ratio (1:0.2). Several variables were next evaluated to determine the factors affecting crystallinity and phase transformations to attempt and achieve a structurally and photocatalytically optimal nanocomposite.
5.1.3.1 Optimizing the H$_2$O:Ti(precursor) Ratio

Preliminary experiments suggested that the effects of the h value ([H$_2$O]:[Ti(OBu)$_4$] ratio) used in the nanocomposite would be more consequential than previously found for pure hydrolyzed TiO$_2$. TiO$_2$-(0.2)ZnFe$_2$O$_4$ alloys were created using h values of 15, 25, 35, and 50. Lower h values were not used, assuming that the photoactivity will rapidly decrease as revealed in Section 5.1.2 for pure TiO$_2$. It was found that, by slowly adding the TiO$_2$-(2wt%)C$_3$H$_7$OH solution to the coprecipitated and amorphous ZnFe$_2$O$_4$ (following the procedure outlined in Figure 4.1) using h values of 15 and 25, relatively homogeneous solutions could be obtained. Using h values of 35 and 50, however, produced agglomerated particles that insufficiently coupled the amorphous TiO$_2$ and ZnFe$_2$O$_4$ precipitates.

Figures 5.11 and 5.12 show the direct relationship displayed between the h value and the anatase-to-rutile ratio found in the composite. Increasing the value of h increased the anatase-to-rutile transformation at calcination temperatures of both 400°C and 500°C. Although the crystal structure of the nanocomposite was determined to be a complex combination of spinel ZnFe$_2$O$_4$, anatase TiO$_2$, and rutile TiO$_2$, as well as small amounts of subproducts, the composition of TiO$_2$ phases were sought to characterize the anatase-to-rutile transformation. Equation 14 was used to estimate the percentage of anatase (as compared to rutile) TiO$_2$ found in the nanocomposites, where $X_A$ is the mass fraction of anatase and $I_A$ and $I_R$ are the X-ray integrated intensities of the (101) reflection of anatase and (110) reflection of rutile, respectively. It should be noted that this equation only takes into consideration the percent anatase and rutile in the formed TiO$_2$ and not of the entire nanocomposite.
The mean crystallite thickness for anatase TiO$_2$, rutile TiO$_2$, and spinel ZnFe$_2$O$_4$ particles were estimated using Scherrer’s equation (Equation 15), where $t$ is the crystallite thickness (nm), $\lambda$ is the wavelength of the X-ray (nm), $B$ is the full width at half maximum (FWHM) of the desired peak, and $\theta$ is the angle at FWHM. It should be noted that calculating particle sizes using Scherrer’s equation is only an estimate, and deviations as great as 60% have been reported due to lack of compensation for instrumental broadening and strains. Scherrer’s equation is therefore used to provide general information about the particle size and only as an aid in drawing experimental conclusions.

$$t = \frac{0.89 \cdot \lambda}{B \cdot \cos \theta_B}$$

(15)

As shown in Table 5.1, increasing the h value from 15 to 50 can increase the anatase-to-rutile transformation by as much as 30%. An h value of 25 was chosen for the remainder of the TiO$_2$-ZnFe$_2$O$_4$ nanocomposite experiments so that a compromise of preparation homogeneity, photocatalytic activity, and maximum anatase crystal structure could be achieved.
Figure 5.11  XRD Spectra of TiO$_2$-(0.2)ZnFe$_2$O$_4$ Calcined at 400° C for $h = [\text{H}_2\text{O}] / [\text{Ti(OBu)}_4]$ (A=Anatase, R=Rutile, $=\text{Spinel ZnFe}_2\text{O}_4$, * = ZnTiO$_3$, # = ZnO).

Figure 5.12  XRD Spectra of TiO$_2$-(0.2)ZnFe$_2$O$_4$ Calcined at 500°C for $h = [\text{H}_2\text{O}] / [\text{Ti(OBu)}_4]$ (A=Anatase, R=Rutile, $=\text{Spinel ZnFe}_2\text{O}_4$, * = ZnTiO$_3$, # = ZnO).
Table 5.1  Structural Data Correlating to TiO$_2$-(0.2)ZnFe$_2$O$_4$ Nanoparticles.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>H</th>
<th>TiO$_2$ – Anatase (%)</th>
<th>Anatase – Mean Particle Size (nm)</th>
<th>Rutile – Mean Particle Size (nm)</th>
<th>ZnFe$_2$O$_4$ – Mean Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>15</td>
<td>41.9</td>
<td>22.1</td>
<td>81.8</td>
<td>111.6</td>
</tr>
<tr>
<td>400</td>
<td>25</td>
<td>37.6</td>
<td>23.7</td>
<td>79.0</td>
<td>113.2</td>
</tr>
<tr>
<td>400</td>
<td>35</td>
<td>18.13</td>
<td>14.51</td>
<td>89.1</td>
<td>110.9</td>
</tr>
<tr>
<td>400</td>
<td>50</td>
<td>11.4</td>
<td>12.7</td>
<td>87.6</td>
<td>96.8</td>
</tr>
<tr>
<td>500</td>
<td>15</td>
<td>32.2</td>
<td>16.9</td>
<td>96.6</td>
<td>59.6</td>
</tr>
<tr>
<td>500</td>
<td>25</td>
<td>19.3</td>
<td>24.3</td>
<td>79.2</td>
<td>62.7</td>
</tr>
<tr>
<td>500</td>
<td>35</td>
<td>11.6</td>
<td>16.9</td>
<td>89.1</td>
<td>57.1</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
<td>6.55</td>
<td>16.8</td>
<td>90.9</td>
<td>65.7</td>
</tr>
</tbody>
</table>

The co-products (ZnO and ZnTiO$_3$) created during the synthesis of the TiO$_2$-ZnFe$_2$O$_4$ nanocomposites were undesirable since they are not thought to enhance charge transfer or separation mechanisms of the overall photocatalytic reaction, based on unfavorable band gaps and band edges. The band-edge positions for all of the primary and co-products are shown in Figure 5.13. An investigation of the nanocomposites composition was conducted using EDS measurements that concluded two results. First, it was determined that the particles were homogeneous in composition by performing repetition measurements across the sample verifying uniformity. Secondly, it was determined that excess zinc was found in the sample (mean content ratio of Fe:Zn = 2:1.4), which explains the extra co-products with compounds containing zinc.
5.1.3.2 Optimizing Molar Concentration of ZnFe$_2$O$_4$

With the determination of the optimum h value needed for TiO$_2$-ZnFe$_2$O$_4$ nanocomposites, the optimum ZnFe$_2$O$_4$ concentration needed to be determined next. The primary objective for this study is to increase the anatase content while maintaining an adequate amount of ZnFe$_2$O$_4$ to create an alloy with the potential of visible light absorption. The fundamental obstacle to alloying ZnFe$_2$O$_4$ with TiO$_2$, however, is that as the concentration of ZnFe$_2$O$_4$ increases, the anatase-to-rutile transformation will begin to occur at a lower onset temperature.
As previously stated TiO$_2$’s irreversible phase transition from anatase-to-rutile occurs by a nucleation-growth process and has no definitive transition temperature since there is no phase equilibria involved [37]. Numerous studies on the anatase-to-rutile transformation of TiO$_2$ have confirmed that the transition is not only dependant upon temperature, but also highly dependant upon the impurity content within the TiO$_2$ lattice. It has been suggested in literature that the anatase-to-rutile transformation involves a collapse of the open anatase structure to a closed rutile structure, instigated by the rupture of two of the six Ti-O bonds of the titanium coordination octahedral (TiO$_{6}^{2-}$) in anatase to form new bonds as the rutile structure [32]. The enhancement of the anatase-to-rutile crystal structure by the alloying of ZnFe$_2$O$_4$ is most probably attributed to the diffusion (during heating) of Fe$^{3+}$ into surface Ti$^{4+}$ forming an oxygen vacancy that promotes nucleation. This substitutional process may occur due to the similar ionic radii for Fe$^{3+}$ (64pm) and Ti$^{4+}$ (68pm), while probably not as conveniently for Zn$^{2+}$ (88pm). Once oxygen vacancies are induced on the surface of the TiO$_2$ lattice by the diffusion of Fe$^{3+}$, it is possible for the vacancies to migrate to the bulk of the TiO$_2$ extending the anatase-to-rutile transformation throughout the lattice. The more Fe$^{3+}$ (and possibly Zn$^{2+}$) available to aid in the creation of oxygen vacancies, the more probable it becomes for rutile formation to occur.

TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites were created for X=0.01, 0.05, 0.1, 0.15, and 0.2. To be consistent in preparation procedures, the pH of the coprecipitated ZnFe$_2$O$_4$ solution was raised to a pH of 6.5 for all samples, which is close to the maximum achievable pH using a 3.5M NH$_4$OH solution for control. Since the amount of NH$_4$OH (70wt% H$_2$O) was different for every sample, the amount of H$_2$O naturally occurring in
the solution varied accordingly. The amount of deionized H$_2$O added to the solution for the hydrolysis of Ti(Obu)$_4$ compensated for the H$_2$O variations attributed to the 3.5M NH$_4$OH solutions used for pH control. An h value of 25 was maintained for reasons provided in Section 5.1.3.1. All samples were calcined at a low temperature of 450°C in a flowing air atmosphere. This temperature was chosen, since TiO$_2$ hydrolyzed from the selected procedure was found to be purely anatase and highly crystalline at this temperature. XRD analysis as displayed in Figure 5.14 shows the rapid enhancement of the anatase-to-rutile transformation as the molar concentration of ZnFe$_2$O$_4$ was increased. For TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites with an X of 0.01 and 0.05, a pure anatase crystal structure was found with particle sizes under 15nm. When X was increased to 0.10, 0.15, and 0.20, the anatase-to-rutile transformation increased rapidly with over 50% rutile crystal structure when X is 0.20. It should also be noticed that ZnFe$_2$O$_4$ peaks could not be discriminated until an X value of 0.15 was used.

![XRD Spectra of TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites Calcined at 450°C for X=0.01, 0.05, 0.1, 0.15, 0.2mol (A=Anatase, R=Rutile, $=$Spinel ZnFe$_2$O$_4$, * = ZnTiO$_3$).](image)

Figure 5.14   XRD Spectra of TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites Calcined at 450°C for X=0.01, 0.05, 0.1, 0.15, 0.2mol (A=Anatase, R=Rutile, $=$Spinel ZnFe$_2$O$_4$, * = ZnTiO$_3$).
Table 5.2 Structural Data Correlating to TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites When X = 0.01, 0.05, 0.10, 0.15, and 0.20 Moles.

<table>
<thead>
<tr>
<th>TiO$_2$-XZnFe$_2$O$_4$ (X, moles)</th>
<th>h</th>
<th>Calcination Temperature (°C)</th>
<th>TiO$_2$ – Anatase (%)</th>
<th>Anatase – Mean Particle Size (nm)</th>
<th>Rutile – Mean Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>25</td>
<td>450</td>
<td>100</td>
<td>14.4</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>25</td>
<td>450</td>
<td>100</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>25</td>
<td>450</td>
<td>72.7</td>
<td>12.7</td>
<td>40.4</td>
</tr>
<tr>
<td>0.15</td>
<td>25</td>
<td>450</td>
<td>54.1</td>
<td>20.4</td>
<td>47.5</td>
</tr>
<tr>
<td>0.20</td>
<td>25</td>
<td>450</td>
<td>47.2</td>
<td>25.3</td>
<td>60.9</td>
</tr>
</tbody>
</table>

UV-Vis (representative of solar) and visible irradiation phenol degradation experiments were performed to evaluate the photocatalytic nature of the TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites. Degradation rates are shown in Figures 5.15 and 5.16, and a breakdown of the degradation rates as a function of UV, UV-Vis, and visible light irradiation is provided in Figure 5.17. It should be noted that the breakdown of the degradation rates comes from UV-Vis and visible light experiments and that the UV degradation is inferred from their difference since the same reactor and conditions are used. There is a slight error, however, that comes from the approximate 8% attenuation caused by the UV-cutoff filter used during visible light experiments. It can be determined from Figure 5.5 that the UV photoactivity of the TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites was found to decrease roughly proportional to the increasing concentration of ZnFe$_2$O$_4$. The visible light photoactivity, however, follows a bell curve with the maximum degradation being achieved with X equal to 0.10. The decreasing
photoactivity for the catalysts when irradiated by UV light is attributed to the increasing formation of rutile with ZnFe$_2$O$_4$ concentrations as well as possible defects in the TiO$_2$ lattice, which may attribute to enhanced EHP recombination. The increased photoactivity of X values of 0.01 to 0.10 can be attributed to the role ZnFe$_2$O$_4$ in extending the photoresponse of the catalyst to visible to short wavelength visible irradiation and effectively transferring charge carriers to particles capable of the appropriate redox reactions. The photoactivity that characterizes the nanocomposite photocatalysts using visible light irradiation is not directly (or at least completely) attributed to ZnFe$_2$O$_4$. The reason for this conclusion is the consistent degradation rates shown in Figure 5.16 as compared with previously determined degradation rates for ZnFe$_2$O$_4$ that were found to cease after short durations. It can also be concluded, from the poor visible light photocatalytic activity of nanocomposites with X equal to 0.15 and 0.20, that TiO$_2$ plays a critical role in the visible light photocatalysis of TiO$_2$-ZnFe$_2$O$_4$ alloys. Although the ZnFe$_2$O$_4$ concentration increases, thereby allowing more charge carriers in response to enhanced visible light absorption, it is thought that the high rutile concentrations impede the overall reaction.
Figure 5.15  UV-Vis Activated Photocatalytic Degradation Rates for TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites.

Figure 5.16  Visible Light Activated Photocatalytic Degradation Rates for TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites.
An Oriel Instruments spectrometer with an integrating sphere was used for UV-Vis spectrometry measurements used to analyze the red-shifts in the absorption regions as a function of ZnFe$_2$O$_4$ alloying concentration. The powders were prepared for spectroscopy measurements by finely grinding them and mixing them in a small solution of H$_2$O, acetyl acetone, and triton X-100 under continuous milling. The molar ratio of the H$_2$O : C$_3$H$_8$O$_2$ : C$_{16}$H$_{26}$O$_2$ solution was respectively 1 : 5.56 : 13.9. The solution was then spin coated at 4000rpm on a glass slide that had been previously cleaned with acetone and dried. The UV-Vis transmittance measurements were taken and converted into absorption readings. The measurements were a function of both the concentration of the film and the transmittance of the film at the respective wavelengths of irradiation. Due to the homogeneous thin film created by spin coating, the difference in the
concentrations between the films was not considered a detriment to the experiment (75-85% transmittance in the pass band regions).

Figure 5.16 displays the absorption readings taken for TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites. It can be seen that the red-shift of the absorption edge is roughly proportional to the ZnFe$_2$O$_4$ alloying concentration. The absorption bands were smooth for low alloying concentrations (X<0.15), however small shoulders appeared for higher ZnFe$_2$O$_4$ concentrations as often seen in the absorption bands of doped photocatalysts.

Figure 5.18 UV-Vis Absorption Measurements for TiO$_2$-(X)ZnFe$_2$O$_4$ Nanocomposites

5.1.3.3 Optimizing Calcination Temperature

The variation of calcination temperatures for most metal oxides significantly affects the particle’s size, crystallinity, and phase content. Although the optimal
calcination temperatures of TiO$_2$ and ZnFe$_2$O$_4$ nanoparticles used for photocatalysis may differ by as much as 250°C as previously addressed in Section 5.1, results have indicated that tailoring to the optimal calcination temperature of TiO$_2$ will be the most beneficial since the anatase phase of TiO$_2$ appears to be playing a critical, although enigmatic, role in the nanocomposite. Because defect concentrations (which for this TiO$_2$ application will lead to oxygen vacancies) typically increase exponentially with temperature, the anatase-to-rutile transformation of TiO$_2$ alloyed with ZnFe$_2$O$_4$ will materialize at lower onset transformation temperatures and possibly even during the amorphous chemical synthesis heating procedures. It will also be determined whether the lower onset temperature will lead to a broader overall transformation rate as a function of temperature.

TiO$_2$-(0.1)ZnFe$_2$O$_4$ nanocomposites were chosen for further experimentation since they have shown the highest properties of visible light photocatalysis and were created using the procedure outlined in Figure 4.1. Four samples were made using identical preparation, stirring, and heating conditions to ensure the highest level of uniformity among samples. The samples were each calcined in a flowing air atmosphere for 3 hours with the first hour being a slowly controlled ramp up to the maximum temperature and the final half hour used for cooling. Calcination temperatures were tested over the range of 400-550°C, not only to characterize the modified anatase-to-rutile phase transformation, but more importantly to determine the calcination temperature and phase formations that provide the optimum visible light photocatalytic activity.
XRD results, as shown in Figure 5.X, revealed that the anatase-to-rutile phase transformation begins at temperatures below 400°C. It can also be safely stated that the overall anatase-to-rutile transformation range has been broadened in conjunction with the lower onset transformation temperature, since at 550°C there is only a 40.6% rutile formation. As shown in Figure 5.X, the maximum photocatalytic activity of the nanocomposites occurred when the alloy was calcined at 450°C. This can be attributed to the low rutile content (~10.8%) and small average particle sizes for both anatase TiO$_2$ and ZnFe$_2$O$_4$.

Figure 5.19  XRD Spectra of TiO$_2$-(0.1)ZnFe$_2$O$_4$ Alloys Calcined at Temperatures between 400-550°C.
Table 5.3 Structural Data Correlating to TiO$_2$-(0.1)ZnFe$_2$O$_4$ Nanoparticles Calcined at Various Temperatures (n.d.- could not be accurately determined from the provided data).

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>H</th>
<th>TiO$_2$ – Anatase (%)</th>
<th>Anatase – Mean Particle Size (nm)</th>
<th>Rutile – Mean Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>25</td>
<td>&lt;100</td>
<td>16.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>450</td>
<td>25</td>
<td>89.2</td>
<td>18.1</td>
<td>40.5</td>
</tr>
<tr>
<td>500</td>
<td>25</td>
<td>62.3</td>
<td>20.2</td>
<td>47.2</td>
</tr>
<tr>
<td>550</td>
<td>25</td>
<td>59.4</td>
<td>27.2</td>
<td>54.6</td>
</tr>
</tbody>
</table>

Phenol degradation experiments (shown in Figure 5.20) conducted using visible light irradiation showed the importance of calcination temperature on the photocatalytic activity of the TiO$_2$-(0.1)ZnFe$_2$O$_4$ nanocomposites. The maximum degradation rate was achieved using a calcination temperature of 450°C. Due to the low calcination temperature, the structure of this alloy was not highly crystalline, and only faint traces of ZnFe$_2$O$_4$ could be identified. It was also observed that, although the nanocomposite calcined at a temperature of 450°C consisted of approximately 11.8% rutile crystal structure, it outperformed the sample calcined at 400°C which was characterized by pure anatase. The low performance of the 400°C sample may be attributed to amorphous ZnFe$_2$O$_4$, and the decrease in photocatalytic performance at temperatures above 450°C may be attributed to the sample’s high rutile content. This conclusion again emphasizes the importance of optimizing the relationship between anatase TiO$_2$ and ZnFe$_2$O$_4$.  

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The optimum TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposite for visible light photocatalysis using the coprecipitated / hydrolysis method under investigation proved to have a ZnFe$_2$O$_4$ alloying concentration of X=10 using a calcination temperature of 450°C. A plot of the optical characteristics of the catalyst versus irradiation conditions (metal halide lamp) is shown in Figure 5.21.
5.2 TiO\textsubscript{2} Doped with Fe\textsuperscript{3+} and Zn\textsuperscript{2+} Ions

As discussed in Section 4.2.2, interest in the past year has increased sharply for the use of TiO\textsubscript{2} co-doped (usually in concentrations of 2wt\% or less) with Fe\textsuperscript{3+} or Zn\textsuperscript{2+} ions or ZnFe\textsubscript{2}O\textsubscript{4} for the purpose of visible light photocatalysis. Experiments provided in literature, however, have not determined if the modified TiO\textsubscript{2} is actually activated by wavelengths corresponding to visible light, or if an increase in solar-activated photocatalysis should rather be attributed to an enhanced UV photoactivity. The experiments following will provide a reference for the visible light activity of co-doped TiO\textsubscript{2} prepared using a sol-gel technique and will also provide procedural limitations that leave the preparation of co-doped TiO\textsubscript{2} in contrast to TiO\textsubscript{2}-ZnFe\textsubscript{2}O\textsubscript{4} alloys.
Sol-gel procedures for the creation of pure and modified TiO$_2$ (powders and films) have been well established, using a wide variety of Ti precursors, solvents, acids, pH conditions, aging times, and thermal treatments. The sol-gel procedure outlined in Figure 4.2 was chosen for its controllability in the presence of both low and high dopant concentrations. Inorganic precursors (Fe[NO$_3$]$_3$·9H$_2$O and Zn[NO$_3$]$_2$·6H$_2$O) for the doping of Fe and Zn were chosen instead of organic precursors (Fe[C$_5$H$_8$O$_2$]$_3$ and Zn(C$_2$H$_5$O$_2$)) based on prior experimental phenol degradation experiments performed by the author. For quantitatively characterizing the dopant concentrations, it was assumed that Fe$^{3+}$ and Zn$^{2+}$ would be the primary dopants instead of ZnFe$_2$O$_4$.

**5.2.1 Optimizing Dopant Concentrations**

TiO$_2$ was chemically doped using molar ratios of TiO$_2$:Fe corresponding to 1:0.06, 0.12, 0.24, 0.6, and 1.2mol%. The molar ratio of Fe:Zn was 2:1 for all experiments. The gelation rate was kept consistent for all dopant concentrations by reducing the quantity of HNO$_3$ (used to stabilize the sol and stabilize the hydrolysis reaction) in order to compensate for the increased acidity caused by the nitrate precursors. Using the procedure outlined in Figure 4.2, 0.8, 0.74, 0.72, 0.65, 0.61, and 0.47 moles of HNO$_3$ were respectively used to equivalently stabilize sols with 0.06, 0.12, 0.24, 0.6, and 1.2mol%Fe. The final pH for each sample was between approximately 0.8 and 0.85, providing gelation times around 12 hours. After another 36 hours of aging, the powders were calcined in a flowing air atmosphere at 500$^\circ$C.

As shown in Figure 5.22, UV-Vis spectroscopy measurements revealed a slight red-shift in the absorption region of the doped catalysts. The absorption bands for the
doped TiO₂ appeared smooth, although shoulders began to develop for higher dopant concentrations (>0.6%). Also shown in Figure 5.22 is a relative plot of the metal halide spectrum. It should be noticed that the baseline is sufficient to irradiate all wavelengths, both UV and visible (>400nm); however, additional irradiation may be absorbed by the TiO₂-(1.2%)Fe catalyst due to the sharp irradiation peak between 400 and 410nm.

![Graph of UV-Vis Absorption Measurements for TiO₂-(X%)Fe Catalysts with a Fe:Zn Ratio of 2:1.](image)

Figure 5.22 UV-Vis Absorption Measurements for TiO₂-(X%)Fe Catalysts with a Fe:Zn Ratio of 2:1.

XRD measurements (Figure 5.23) show that the doped photocatalysts consist primarily of anatase particles when calcined at 500°C. A slight trace of rutile’s (110) reflection plane, which occurs at a 2 theta angle of approximately 27.5°, can be observed for the higher crystallinity doped samples with X values of 0.06 and 0.12%. The average particle size as calculated by Scherrer’s equation was between 8.8 and 14.5nm, with the
particle size decreasing with the decreasing crystallinity emanating from high dopant concentrations.

Figure 5.23 Sol-gel Prepared TiO$_2$-(X)Fe with a Fe:Zn Ratio of 2:1.

The photocatalytic activity of the catalysts was analyzed using UV-Vis and visible light phenol degradation experiments. The published literature on the photoactivity of TiO$_2$ co-doped with Zn and Fe or ZnFe$_2$O$_4$ suggests that the photocatalytic activity is enhanced over that of pure TiO$_2$ when irradiated by UV or solar light, although the visible light response of the catalyst is unknown [72, 73]. In contrast to experimental studies in literature, Figure 5.24 shows that all dopant concentrations reduced the photoactivity when irradiated by UV-Vis light. Visible light photocatalysis experiments revealed slight visible light (>400nm) photoactivity for all doped samples with a maximum degradation of 8.55% in 105 minutes when using a TiO$_2$-(0.24%)Fe
catalyst. From Figure 5.26, it can be concluded that the UV photoactivity of TiO$_2$ is decreased in Fe and Zn co-doped samples, while visible light photoactivity may be attained.

The low visible light photoactivity rates for the co-doped catalysts should not be attributed completely to the relatively small addition of photons their humble absorption shift commissions. This recommendation is made because the visible light photoactivity of the co-doped samples begins to decrease as the doping concentrations continue to increase. For example, the extended absorption region of the TiO$_2$-(1.2%)Fe co-doped sample allows the catalyst to absorb the intense 400-410nm irradiation peak from the metal halide lamp, although its visible light photoactivity is only one-third of the TiO$_2$-(0.24%)Fe co-doped sample. The photocatalytic efficiency therefore decreases significantly with dopant concentrations greater than the optimal value (X=0.24%). Although this phenomenon has not been explained in detail, suggestions are often made that the decrease in photocatalytic efficiency caused by an excess of metal ion doping can be attributed to the competition for photons between the metal ions and TiO$_2$. This suggestion, however, is dependant upon the location of the metal ions in or on the TiO$_2$ lattice. If small radii metal ion dopants such as Fe$^{3+}$ are substituted for Ti$^{4+}$, the result may be a decrease in crystallinity of the TiO$_2$ lattice and extended absorption region, as can be seen by the XRD results in Figure 5.23.
Figure 5.24  UV-Vis Light Phenol Degradation Rates for TiO$_2$-(X\%)Fe with a Fe:Zn Ratio of 2:1.

Figure 5.25  Visible Light Phenol Degradation Rates for TiO$_2$-(X\%)Fe with a Fe:Zn Ratio of 2:1.
5.2.2 Effects of Sulfation on \( \text{Fe}^{3+} \) and \( \text{Zn}^{2+} \) Co-doped TiO\(_2\) Photocatalysts

One potential method of increasing the photocatalytic activity of TiO\(_2\) is to increase the number and strength of its surface acid sites through impregnation by SO\(_4^{2-}\) ions. Sulfation procedures have attracted a great deal of interest over the last decade by providing metal oxide catalysts with characteristics equated with strong acid catalysts. Although the most common sulfated oxide is SO\(_4^{2-}/\text{ZrO}_2\), other catalysts have been created such as SO\(_4^{2-}/\text{TiO}_2\), Fe\(_2\)O\(_3\), SnO\(_2\), SiO\(_2\), Al\(_2\)O\(_3\), and HfO\(_2\) [82]. These sulfated catalysts are usually created by impregnating amorphous metal oxide particles in a sulfating solution of diluted (usually 1M solution) H\(_2\)SO\(_4\) or (NH\(_4\))_2SO\(_4\), depending upon the reactive properties of the metal oxide precursors. Amorphous metal oxide particles are used instead of crystalline particles to maximize the amount of adsorbed SO\(_4^{2-}\) ions,
and the following calcinations at high temperatures are said to produce a highly covalent sulfate structure on the particle’s surface [83]. The ideal sulfur content for doping is suggested to be in the range of 1-2wt% [82]. Although the sulfation process is known to enhance the photocatalytic properties of a photocatalyst such as TiO$_2$ by increasing surface adsorption strengths, physical properties may also be enhanced. For SO$_4^{2-}$/TiO$_2$ catalysts, for example, the metastable anatase phase may be stabilized at higher calcination temperatures, and the particle size may be reduced coinciding with an increased surface area.

Sulfur impregnated TiO$_2$-(X)Fe photocatalysts with a Fe:Zn ratio of 2:1 were created using the procedure outlined in Figure 5.27. The objective of this experiment was to improve the visible light photocatalytic activity of the co-doped TiO$_2$ by increasing the number and strength of the surface acid sites and by increasing the catalyst’s surface area. The same sol-gel procedure was used as in Figure 4.2; however, the amorphous co-doped particles obtained after drying were impregnated in a 1M H$_2$SO$_4$ solution for 1 hour using 50mL of solvent per gram of catalyst. The sulfated particles were then filtered, dried, and calcined at 500°C.
Figure 5.27  Sol-gel Impregnation Procedure for Co-doped TiO$_2$/SO$_4^{2-}$.

XRD measurements (Figure 5.28) show that the SO$_4^{2-}$ impregnated and co-doped TiO$_2$ photocatalysts calcined at 500°C consist solely of anatase particles, regardless of the doping concentration. The mean particle size for the impregnated samples was between 9.8 and 14.8nm in comparison to the 8.8 to 14.5nm mean particle sizes found for the non-impregnated samples. The comparable particle sizes between impregnated and non-
impregnated samples are attributed to the low calcination temperature in conjunction with the metal ion dopants that impede crystallinity.

Figure 5.28  Sol-gel Prepared TiO$_2$-(X)Fe with a Fe:Zn Ratio of 2:1 and Impregnated with SO$_4^{2-}$ Ions.

The photocatalytic activity of the SO$_4^{2-}$ impregnated catalysts was analyzed using UV-Vis and visible light phenol degradation experiments (as shown in Figures 5.29 and 5.30). The UV-Vis photocatalytic activity between sulfated and non-sulfated catalysts was found to be roughly the same. Any increase in photoactivity of the sulfated samples can likely be attributed to the strengthened acid sites on the catalyst’s surface, since the particle size and phase transitions were negligible due to preparation conditions. The most notable contribution of SO$_4^{2-}$ impregnation using the chosen synthesis conditions
was the increased visible light photoactivity at a sacrifice to the UV photoactivity. As shown in Figure 5.29 and 5.30, for co-doping concentrations greater than \( X=0.24\% \) with a Fe:Zn ratio of 2:1, the visible light photoactivity approaches that of the UV photoactivity.

Figure 5.29  UV-Vis Phenol Degradation Rates for \( \text{SO}_4^{2-} \) Impregnated \( \text{TiO}_2-(X\%) \text{Fe} \) with a Fe:Zn Ratio of 2:1.
Figure 5.30  Visible Light Phenol Degradation Rates for SO$_4 ^{2-}$ Impregnated TiO$_2$-(X%)Fe with a Fe:Zn ratio of 2:1.

Figure 5.31  Breakdown of the Phenol Degradation Characteristics for SO$_4 ^{2-}$ Impregnated and Non-impregnated TiO$_2$-(X%)Fe Nanocomposites with a Fe:Zn Ratio of 2:1 when Irradiated by UV, UV-Vis, and Visible Light.
To thoroughly evaluate the effects of $SO_4^{2-}$ impregnation on Fe and Zn co-doped TiO$_2$, various calcination temperatures were used to alter the crystallinity, phase transformations, and particle sizes. A moderate calcination temperature of 500°C was previously chosen for the co-doped catalysts, since it produced crystalline TiO$_2$ characterized by a pure anatase structure. If the calcination temperature is increased from 500°C to 600°C (as shown in Figure 5.34), the anatase-to-rutile phase transformation rapidly occurs, with the estimated rutile content changing from 0% to 94.2%, respectively.
By impregnating the Fe and Zn co-doped catalysts with SO$_4^{2-}$, it is possible to stabilize the anatase crystal structure of the TiO$_2$ at higher temperatures and therefore also increase the crystallinity of the sample. XRD measurements, provided in Figure 5.35, show that the anatase crystal structure can be completely stabilized at temperatures as high as 600°C and crystallinity can be subsequently enhanced. The mean crystal size of the anatase particles increases from approximately 10.1nm to 29.8nm when calcination temperatures increase from 500°C to 600°C. UV-Vis and visible light phenol degradation experiments were performed for SO$_4^{2-}$ impregnated co-doped TiO$_2$ samples calcined at temperatures of 500, 550, and 600°C. Results concluded a negligible impact of calcination temperature on photoactivity. Several possible explanations exist for this
conclusion. First, as the calcination temperature is increased, the mean particle size increases significantly (10.1nm-29.8nm), thereby lowering the surface area of the catalyst. Secondly, the strength of the surface acid sites on the surface of the TiO$_2$ is not expected to increase with calcination temperature, therefore negating additional benefits relating to strong acid catalysts.

![Graph showing X-ray diffraction patterns at different calcination temperatures](image)

Figure 5.35  Sol-gel Prepared SO$_4^{2-}$ Impregnated TiO$_2$-(0.24%)Fe with a Fe:Zn Ratio of 2:1 at Various Calcination Temperatures.
Table 5.4  Structural Data Correlating to TiO₂-(0.24%)Zn Nanoparticles with a Fe:Zn Ratio 2:1 and Various Calcination Temperatures.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>SO₄²⁻ Impregnation</th>
<th>TiO₂ – Anatase (%)</th>
<th>Anatase – Mean Particle Size (nm)</th>
<th>Rutile – Mean Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>No</td>
<td>100</td>
<td>11.2</td>
<td>-</td>
</tr>
<tr>
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<td>No</td>
<td>55.6</td>
<td>20.2</td>
<td>69.6</td>
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<td>No</td>
<td>15.8</td>
<td>28.9</td>
<td>171.5</td>
</tr>
<tr>
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<td>Yes</td>
<td>100</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>550</td>
<td>Yes</td>
<td>100</td>
<td>20.2</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>Yes</td>
<td>100</td>
<td>29.8</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions for TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites

The objective of this project was to create a nontoxic, stable, and inexpensive catalyst that could be activated by visible light (>400nm). A new coprecipitation/hydrolysis method was created to effectively couple TiO$_2$ and ZnFe$_2$O$_4$ -- two photocatalysts that typically require discrepant preparation procedures and conditions. TiO$_2$ and ZnFe$_2$O$_4$, functioning alone, were found to have negligible photoactivity in response to visible light; however, functioning as a nanocomposite, photoactivity was accomplished relative to the optimization of preparation conditions.

The visible light photoactivity of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites was found to be a function of the water-to-alkoxide precursor ratio, ZnFe$_2$O$_4$ concentration, and calcination temperature. Other parameters that were modified, although not mentioned in this study, include the pH and temperature of the preparation solution, Zn and Fe precursors (organic versus inorganic), and the base used for controlling the pH. Through optimization of the above preparation parameters, structural properties such as phase formation, crystallinity, and particle size of the nanocomposite could be optimized.

This project also attempted to unveil some of the mystery regarding the reaction mechanisms of coupled semiconductor photocatalysts that are not clearly identified as
photosynthesizers, such as in the case of TiO$_2$-CdS or TiO$_2$-WO$_3$. From experiments outlined in Chapter 5, several conclusions can be made about the coupling of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites as prepared by the synthesis procedure under investigation. First, it was determined that ZnFe$_2$O$_4$ was necessary for visible light photoactivity, although it was not the exclusive source. Results outlined in this project imply an essential correlation between the metastable anatase phase of TiO$_2$ and ZnFe$_2$O$_4$. Any charge transfer mechanism for this composite, however, is enigmatic at best, since the conduction band-edge energy level of crystalline ZnFe$_2$O$_4$ is slightly unfavorable for the reduction of O$_2$. In addition, the band-edge energy levels of TiO$_2$ and ZnFe$_2$O$_4$ suggest that the nanocomposite can not function as a visible light synthesizer, since both the conduction and valance band edges of ZnFe$_2$O$_4$ are lower in energy than the respective band edges of TiO$_2$.

Consistent results showing the inactivity of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites with a rutile mass fraction greater than 15%, suggest that anatase TiO$_2$, although incapable of absorbing wavelengths longer than 380nm, serves a primary role in the photoactivity of the nanocomposites. This experimental conclusion suggests a puzzling charge transfer phenomena existing between anatase TiO$_2$, ZnFe$_2$O$_4$, and possibly even small molar fractions of nanosized co-products produced using coprecipitation/hydrolysis method. Another possible explanation, however, can be drawn from consistent results that suggest optimal visible light photoactivity is achieved with anatase particles less than approximately 15nm coupled with ZnFe$_2$O$_4$ of low-crystallinity. It may be possible that intimately coupled particles with dimensions close to quantum-sizes experience effects which promote photocatalysis at wavelengths absorbed by the near-amorphous ZnFe$_2$O$_4$.
particles. If Q-effects are indeed involved, it may also be possible that ZnFe$_2$O$_4$ nanoparticles of low crystallinity prepared at low calcination temperatures may experience a band gap increase of one to several tenths of an electron volt, thereby reducing the energy level of the conduction band edge to a potential that can effectively reduce O$_2$.

Despite the cogitation concerning the reaction mechanisms of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites, it was determined that visible light photoactivity could be attained by optimizing the preparation conditions and structural characteristics of the photocatalysts. The increase in visible light photoactivity, however, was achieved at the expense of the UV photoactivity displayed by pure TiO$_2$ nanoparticles (as outlined in Figure 5.X). The reduction in UV photoactivity, which contravenes solar photocatalysis, is thought to be caused primarily by lattice distortions and substitutional impurities by Fe$^{3+}$ ions in the TiO$_2$ lattice, and secondly because of the competition between TiO$_2$ and ZnFe$_2$O$_4$ nanoparticles. Figures 6.1 and 6.2, respectively, compare the photoactivity of a TiO$_2$-(0.1)ZnFe$_2$O$_4$ photocatalyst with that of Aldrich’s pure anatase TiO$_2$ in response to UV and visible light irradiation.
Figure 6.1 UV Phenol Degradation Rates for TiO$_2$-(0.1)ZnFe$_2$O$_4$ Nanocomposites.

Figure 6.2 Visible Light Phenol Degradation Rates for TiO$_2$-(0.1)ZnFe$_2$O$_4$ Nanocomposites.
6.2 Conclusions for Fe and Zn Co-doped TiO$_2$

A secondary objective for this project (in attempts to thoroughly evaluate the influences of Zn and Fe on the photoactivity of TiO$_2$ through ion doping or oxide alloying) was to determine the effect of Fe and Zn co-doping on the visible light photoactivity of TiO$_2$. A common sol-gel technique was used to create the TiO$_2$-(X\%)Fe catalysts with an Fe:Zn ratio of 2:1 and X values of 0.06, 0.12, 0.24, 0.6, and 1.2\%. Photocatalytic studies using phenol degradation showed that, despite the humble absorption edge red-shifts, the co-doped catalysts were photoactive for wavelengths longer than 400nm. Fe and Zn co-doped TiO$_2$ was also impregnated with SO$_4^{2-}$ ions, which proved to increase the visible light photoactivity of the co-doped samples by an average of 35\% over the 105-minute irradiation period. As with alloyed TiO$_2$-ZnFe$_2$O$_4$ nanocomposites, the photoactivity of the co-doped TiO$_2$ could extend the photoresponse of the catalyst, but at the expense of the overall solar irradiated photoactivity.

6.3 Recommendations

The field of visible light photocatalysis is growing exponentially and research topics and ideas are broadening, mainly because the informational theory behind many photocatalytic reactions lags behind experimental results. The coupling of semiconductor photocatalysts is no exception, as a wide array of structural and physical properties remain in question.

TiO$_2$-ZnFe$_2$O$_4$ nanocomposites should continue to be pursued because of the lack of inexpensive and currently known visible light (besides mere 0.1-0.3eV band gap alterations) absorbing alternatives. Physical properties such as charge transfer
mechanisms, the critical nature of ZnFe$_2$O$_4$’s particle size, and the role of TiO$_2$’s anatase crystal structure must be conclusively determined. Procedural properties must also be thoroughly investigated, such as the effects of Ti precursors, hydrolysis methods, and the effects of particle interaction using mechanochemical processes on amorphous TiO$_2$-ZnFe$_2$O$_4$ particles prior to calcination.

Since the anatase phase of TiO$_2$ was found to have a direct, although uncertain, correlation with the photoactivity of the nanocomposites, advanced hydrolysis methods should be sought to enhance its photocatalytic properties. If the UV photoactivity of the hydrolyzed pure TiO$_2$ can be increased, the role of TiO$_2$ may be more accurately determined if it is found that the photoactivity enhancement extends to visible wavelengths during the creation of nanocomposites.

Since the absorption edge of metal ion co-doped catalysts is limited to several tens of nanometers, these photocatalysts may find their most promising role in solar irradiated photocatalytic reactions. A vast number of sol-gel techniques have been successfully created and utilized for the creation of homogeneous TiO$_2$ with high purity. Various preparation methods should be implemented not only to maintain, but also to enhance, the photocatalytic activity of TiO$_2$ in response to UV irradiation, while adding the visible light photoactivity achieved from co-doping to achieve a synergistic effect for solar irradiation.
REFERENCES


