Novel Nanostructures And Processes For Enhanced Catalysis Of Composite Solid Propellants

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NOVEL NANOSTRUCTURES AND PROCESSES FOR ENHANCED CATALYSIS OF COMPOSITE SOLID PROPELLANTS

by

ROBERT DRAPER
B.S.M.E. University of Central Florida, 2012

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term
2013
The purpose of this study is to examine the burning behaviour of composite solid propellants (CSP) in the presence of nanoscale, heterogenous catalysts. The study targets the decomposition of ammonium perchlorate (AP) as a key component in the burning profile of these propellants, and seeks to identify parameters of AP decomposition reaction that can be affected by catalytic additives. The decomposition behavior of AP was studied in the presence of titanium dioxide nanoparticles in varying configurations, surface conditions, dopants, morphology, and synthesis parameters with the AP crystals. The catalytic nanoparticles were found to enhance the decomposition rate of the ammonium perchlorate, and promote an accelerated burning rate of CSP propellants containing the additives. Furthermore, different configurations were shown to have varying degrees of effectiveness in promoting the decomposition behaviour.

To study the effect of the catalyst’s configuration in the bulk propellant, controlled dispersion conditions of the nanoparticle catalysts were created and studied using differential scanning calorimetry, as well as model propellant strand burning. The catalysts were shown to promote the greatest enthalpy of reaction, as well as the highest burn rate, when the AP crystals were recrystallized around the nanoparticle additives. This is in contrast to the lowest enthalpy condition, which corresponded to catalysts being dispersed upon the AP crystal surface using bio-molecule templates.

Additionally, a method of facile, visible light nanoparticle tracking was developed to study the effect of mixing and settling parameters on the nano-catalysts. To accomplish this, the titania nanoparticles were doped with fluorescent europium molecules to track the dispersion of the catalysts in the propellant binder. This method was shown to successfully allow for dispersion and agglomeration monitoring without affecting the catalytic effect of the TiO$_2$ nanoparticles.
ACKNOWLEDGMENTS

I would like to thank Dr. Seal, and the entire group at the Surface Engineering and Nanotechnology lab for their continued support, insight, and constant willingness to assist others.
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Propellants are chemical systems which have a propensity to release energy such that a fluid is thrust as a means toward propelling an object. Propellants can be characterized into two overarching categories: liquid and solid, although propellants can be found in gaseous, gelled, or liquid-solid hybrid configurations as well. Both propellant categories operate using the same basic principles and components, but the differing configurations lead to vastly different properties and performance. Both types of propellants in their basic form contain a flammable fuel, and an oxidizing compound to facilitate the combustion reaction[1]. Liquid propellants use liquid fuels, such as liquid hydrogen or kerosene, in conjunction with a liquid oxidizer, such as liquid oxygen or red fuming nitric acid[1][38][19]. Liquid fuels have advantageous properties, in that they are highly tunable by controlling the liquid flow rates, thereby allowing for variable thrust and the ability to halt or restart the reaction. Liquid fuels also tend to have a high power density, and their low weight enables the use of lighter fuel tanks[1][38]. Despite these advantages, liquid fuels provide instability due to the complexity and fragility of the propellant system. Typically, liquid propellants require the oxidizer to be cryogenically cooled, and also require complex pumping systems to move the fuel to the ignition source at the desired rate. These systems add complex dependencies to the propellant system, increasing the number of possible single points of system failure[38]. To contrast, solid propellants are often much simpler systems, in the most basic sense comprising of a flammable solid. This solid propellant can be a monophasic, burnable solid such as blackpowder or nitrocellulose, or it can consist of multiple solid components incorporated into a composite structure. Solid propellants thus tend to require less complex systems to make the reaction proceed, and have an added advantage of durability. However, solid propellants tend to be less tunable, having difficulties throttling or halting the reaction mid flight[38].

Within the solid propellant category, composite solid propellants (CSP) have historically pro-
moted wide industrial interest due to the tunability gained from varying single components in the composite propellant system. CSP in their general, simplest form are composed of a solid fuel, oxidizer, and binder[1]. The fuel is typically a metal powder, either made of magnesium or aluminum[48][19]. The oxidizer in a solid propellant is a crystalline compound with a high propensity to donate oxygen to the metal fuel. The binder is usually a rubber derivative in which the fuel and oxidizer are embedded, cast and cured into a solid burnable component. Frequently, other additives, such as plasticizers, or catalysts will be added to change the mechanical or chemical performance of the propellant. However, within even the most basic configuration, the propellant can vary widely depending on which chemical compounds are being used as the fuel, oxidizer, and binder, as well as the solid morphology that the compounds are in. Being that the CSP is in a solid configuration, the reaction kinetics are affected by many of the properties of the solid constituents. For the energetic reactions to take place, species from the oxidizer crystals must be transported to the site of the reacting metal at a rate fast enough to propel the reaction. As such, the dispersion of the propellant constituents, as well as the decomposition parameters of the oxidizer crystals play a large role in the performance of the overall propellant. One of the methods of increasing the performance of the propellant is to speed up the decomposition of the oxidizer crystals, as it can be the limiting component in the propellant reaction. This is commonly achieved through the addition of a catalyst to either lower the activation energy required for decomposition, or alter the reaction of the species given off by the oxidizer crystals[48].

Recent interest and ability to design and study nano-scaled solid particles has significantly affected the effectiveness and tailorability of the heterogenous catalysts used in CSP. As catalytic mechanisms frequently are affected by the active surface area of the solid catalyst, utilizing nanoparticle catalysts can allow for CSP with significantly accelerated performance in terms of burning rate, specific impulse, and tunability. In the present study, the goal was to investigate the role that nanoparticulate solid state catalysts play in the decomposition of oxidizer crystals. The most
commonly used solid oxidizer used in composite propellants is ammonium perchlorate, and was thusly chosen as the model upon which to investigate the mechanisms for solid state catalysis. The present study investigated the catalytic effect in two main phases: creation of novel dispersion and interfacial coordinations, and the development of a facile dispersion monitoring system.

The dispersion monitoring capabilities were created by inducing luminescence in catalytic nanoparticles, enabling visible-light monitoring of their dispersion, agglomeration, and settling. This system greatly simplifies the process and equipment needed to monitor nanoparticle dispersion and agglomeration in a bulk system, and allows the catalytic activity of the nanoparticles to be maintained. Meanwhile, the novel interfacial coordinations were created through the use of bioconjugate pairs to allow the catalytic nanoparticles to be templated into configurations that would be otherwise difficult or unachievable. These new dispersion configurations would allow for the study of interfacial mechanisms between the catalyst and the oxidizer. They would also enhance the study of the effect of catalyst proximity to the reaction site.
Ammonium perchlorate, is a white crystalline salt with an orthorhombic structure at ambient temperature and pressure shown in Figure 2.1 [5].

![Figure 2.1: Illustration of the crystal faces of an ammonium perchlorate crystal. a:(1 0 0); c: (0 0 1); m: (1 1 0); r: (1 0 2); q: (0 1 1)[5]](image)

However, at a temperature greater than 240 °C, the crystal starts to transition to a cubic structure, shown in Figure 2.2.

![Figure 2.2: Polymorphous transition in ammonium perchlorate crystals in the plane (0 0 1)[5]](image)

At ambient pressure, the material sublimes around 300 °C [21]. This sublimation is limited at this temperature range, usually leading to a 30% volumetric reduction, but producing a residue on
the surface of the AP crystal. The residue generated is itself composed of ammonium perchlorate with identical chemical composition to that of the bulk crystal, but in a morphology with significantly higher surface area. With additional temperature increases at ambient temperature, the interfacial residue also sublimes. The energy rate for this ambient pressure sublimation is around 21 kcal/mole[21]. With increasing pressure this sublimation process is replaced with thermal decomposition. It is proposed that this decomposition involves the dissociation of AP in ammonia and perchloric acid whereupon they evaporate. In the gas phase, the perchloric acid decomposes, and the ammonia is oxidized, shown in Equation 2.1. Upon decomposing, many subreactions can occur, some of which are shown in 2.1. This phase of the AP decomposition has an activation energy of 39 kcal/mole. These values have been obtained with respect to AP in inert gas conditions. However, it has been seen that the thermal decomposition of AP is relatively unaffected by the presence of molecular oxygen, and as such are representative of an AP system decomposing in atmosphere.

\[ NH_4^+ + ClO_4^- \rightleftharpoons NH_3(a) + HCl_4(a) \]

\[ HCl_4 \rightleftharpoons OH^- + ClO_3^- \]

\[ 2OH^- \rightleftharpoons H_2O(g) + \frac{1}{2}O_2(g) \]  \hspace{1cm} (2.1)

\[ 2ClO_5^- \rightarrow Cl_2 + 3O_2 \]

\[ 2NH_4ClO_4 \rightarrow 4H_2O + Cl_2 + O_2 + 2NO \]

Additionally, traces of $HClO_4$, $Cl_2$, $N_2O$, $O_2$, $N_2$, $H_2O$, $HCl$, $ClO_2$, $NOCl$ were found in the reaction products. Other reaction products, such as nitric acid, and NO can evolve during the reaction process, but are contingent upon certain decomposition ranges and temperatures.
When combined with the mechanical stresses and dislocation motion induced in the AP decomposition process, the following decomposition feedback process, shown in Figure 2.3 occurs[5].

The decomposition process of the AP crystals can be largely affected by the surrounding gaseous conditions, including species that have sublimated or been gassed off from the crystal surface. The model for the diffusion of species can be derived from the kinetics of a simple contracting surface shown in Equation 2.2, where \( \alpha \) is the fractional decomposition of residue, and \( \gamma = 2 \) or 3 depending on the pressure.

\[
1 - (1 - \alpha)^{\frac{1}{\gamma}} = kt
\]

Figure 2.3: Feedback contour of the AP decomposition process[5]
In the steady state, the flux of gaseous ammonia and perchloric acid must be equal.

\[ J_A = -D_A \left( \frac{\delta n_A}{\delta r} \right) = -D_P \left( \frac{\delta n_P}{\delta r} \right) \]  \quad (2.3)

Assuming spherical symmetry of the AP crystals, the kinetic equation becomes the equation below, where

\[ \frac{\delta n}{\delta t} = \frac{D}{r^2} \frac{\delta}{\delta r} (r^2 \frac{\delta n}{\delta r}) \]  \quad (2.4)

The solution to the steady state component of this equation is of the form below

\[ n = A + \frac{B}{r} \]  \quad (2.5)

Considering the boundary conditions, the flux becomes

\[ J = \frac{D a n_0}{r^2} \]  \quad (2.6)

In the Fuchs model, we assume that molecules from the AP crystal evaporate from the crystal surface and are not affected by molecules in the gas phase until they travel some distance \( \Delta \) that is a function of the mean free path, whereupon they will undergo collisions. With these conditions, Equation 2.4 gives a rate, \( Q \), in the equation below

\[ Q = 4\pi (a + \Delta)^2 J = \frac{4\pi D a n_0}{\frac{D}{a^2} + \frac{a}{a + \Delta}} \]  \quad (2.7)

This model shows that there is a kinetic relation between the particle diameter \( a \), as well as an
additional radial component from the mean free path before collision $\Delta$, and the diffusivity and mean velocity of the sublimating molecules. The kinetic underpinnings of the decomposition of the solid oxidizer compound can greatly affect the nature of catalytic mechanism that will occur during the differing pressure/temperature regimes.

Catalysts for Ammonium Perchlorate Decomposition

*Metal Additives*

Chaturvedi et al. have conducted a review on the usefulness of metallic nanoparticles as catalysts for AP decomposition[7]. The authors report that the addition of Ni, Cu and Al powders on the nanoscale produces a lowered AP high temperature decomposition (HTD) by 112.9 °C, 130.2 °C, and 51.8 °C respectively[7]. Thus, the authors conclude that the metal nanoparticle have a high propensity to catalyze the exothermic decomposition of AP. When comparing the low temperature AP decomposition (LTD) the addition of nanometer Cu decreased the exothermic peak by 35.1 °C, while the Ni and Al powders increased the peak by by 3.9 °C and 5.9 °C respectively. Out of the surveyed nanometal powders, only copper powder reduced the AP LTD, while the nickel and aluminum powders increase the peak exothermic temperature. Additionally, the authors noted that the total DTA heat releases of AP in the presence of nanometer Ni, Cu and Al were 1.32 kJ/g, 1.20 kJ/g and 0.903 kJ/g, respectively, which are all significant increases over uncatalyzed AP. Reinforcing this catalytic tendency of metallic nanoparticles, Duan et al. have shown that nanoscaled nickel has a significant catalytic effect on the decomposition of AP[10]. Compared with the thermal decomposition of pure AP, adding Ni nanoparticles (25 wt.%) in AP decreases its decomposition temperature by 92-105 °C and increases its apparent decomposition heat by 787.1-796.1 J/g, assessed using thermogravimetric methods. In addition to investigating single metal catalysts, the authors also investigated bi-metallic alloys to catalyst the AP decomposition
reactions. It was shown that the decomposition temperature of AP was decreased by 140.4 °C in when catalysed by NiCu powder, which is a more significant than either Ni or Cu powder alone. The mechanism of thermal decomposition of AP in the presence of these metallic catalysts was suggested to occur through a proton transfer mechanism. Ping et al. have shown that the addition of carbon nanotubes (CNT) can additionally increase the catalytic behvaior of the metallic particles. Using Cu/CNT composite particles, the AP HTD peak temperature decreased by 126.3 °C. When compared with Cu, the HTD peak temperature of the AP-Cu/CNT composite is decreased by 20.9 °C, indicating that metallic composites can also act as effective catalysts for the AP decomposition reactions.

_Metal Oxide Additives_

Many studies have shown the promising use of metal oxides in accelerating the decomposition process for Ammonium Perchlorate. The most simplistic form of a heterogenous oxide catalyst for AP decomposition would be a single metal oxide. Often, transition metal oxides provide a p-type semiconductor suitable to accelerate one or more of the rate limiting steps of the thermal decomposition process. The catalytic effect can sometimes be expressed in the form of a lowered activation energy for combustion, or in the lowering of the decomposition temperatures of AP. Additionally, some additives can serve to increase the enthalpy of reaction for AP, causing an overall burning rate increase in the CSP.

Gheshlaghi et al. have suggested that mixed metal oxide nano powders have a high propensity to advance the catalytic effect of AP[2]. They address the two main mechanisms of AP decomposition: electron transfer, and proton transfer. In the electron transfer process, an electron is
transferred from the perchlorate ion to the ammonium ion as follows:

\[
ClO_4^- + NH_4^+ \rightarrow ClO_4^0 + NH_4^0
\]  
(2.8)

\[
NH_4^0 \rightarrow NH_3 + H
\]
(2.9)

\[
ClO_4^0 + ClO_4^- = ClO_4^- + ClO_4^0
\]
(2.10)

\[
HClO_4 + H \rightarrow H_2O + ClO_3
\]
(2.11)

In this process, it has been proposed that the electron transfer is the rate limiting step. As such, catalytic oxides can accelerate the decomposition process by expediting the electron transfer as follows:

\[
e^{-}_\text{oxide} + ClO_4^- \rightarrow O_\text{oxide} + ClO_3^- \rightarrow \frac{1}{2}O_2 + ClO_3^- + e^{-}_\text{oxide}
\]
(2.12)

For this process to be facilitated, a p-type semiconductor with effective positive hole sites on the surface would be needed to accept the electron released from the perchlorate ion.

In the second process, a proton is transferred from the ammonium ion to the perchlorate ion, as shown:

\[
NH_4ClO_4(s) \rightarrow NH_4^+ + ClO_4^- \rightarrow NH_3(s) + HClO_4(s) \rightarrow NH_3(g) + HClO_4(g)
\]
(2.13)
The positive hole in Equation 2.12 $e^-_{oxide}$ in the oxide valance band, and the abstracted oxygen $O_{oxide}$ are the contributing altering factors in accelerating the electron transfer process.

The authors go on to state that the electron transfer mechanism involves two steps: ammonia oxidation and $ClO_4^-$ dissociation into $ClO_3^-$ and $O_2$. During the ammonia oxidation step, metal oxides tend to show high catalytic behavior in oxidating the ammonia species. In the chlorate decomposition step, the metal oxide can accept a donated electron from the oxidation step, which facilitates the perchlorate decomposition into chlorate and molecular oxygen.

The authors assert that the spinel type mixed metal oxide $CuCo_2O_4$ has a significantly increased catalytic effect over other metal oxide catalysts. As a proposed explanation, the authors that the partially filled 3d orbital of Cu$^{2+}$ and Co$^{3+}$ allow for a situation where the copper and cobalt ions can readily accepted the electron released from the perchlorate ion to form a filled, stable 3d orbital. The authors attribute the presence of two sets of unfilled 3d orbitals to a ”synergistic catalytic effect.” Wang et al. have also shown a synergistic catalytic effect through the use of a nanoscaled copper oxide and iron oxide composite[60].

Due to the complexity of the propellant system, and the number of ways that the reactants and products can interact, it can become difficult to predict the nature of the interaction between a catalyst and the AP oxidizer. As such, Hedmen et al. used a high speed, planar induced laser fluorescence (PLIF) setup, coupled with a microscopic imaging system to visually investigate the decomposition mechanisms, and the nature of metal-oxide catalyst interactions. Reported values for the decrease in ignition temperature vary significantly for CuO/AP mixtures [22]. This is because the ignition temperature depends on many factors including mass of the reactant, concentration of catalyst, heating rate, and how the AP/catalyst mixture was combined. CuO is known to be particularly effective in decreasing ignition temperature of AP and has been the subject of several catalysis studies[8][65], as well as ignition studies [17][30]. These studies report that CuO
lowers the ignition temperature of AP by 95-170 K, which accounts for some of the decrease in ignition delay times that have been observed. With those mechanisms noted, there are some reasons why a lowering of the ignition temperature would be the only mechanism that accounts for the ignition delay decrease. In the reported studies, the samples were tested in ways that were incongruent with a CSP ignition procedure. The temperature of ignition in the AP/CuO composites used catalyst concentrations well above a typical CSP additive level, and heated the samples slowly and constantly[17]. It is likely that the ignition delay would be much less pronounced in a true CSP system.

Meanwhile, some studies indicate that the mechanism is from the acceleration of the fine AP/binder mixture burning rate [6][4]. This mechanism would cause a higher degree of protrusion of coarse AP crystals beyond the CSP surface resulting in more of the AP particle surface being exposed to the reacting gas phase, which could decrease the ignition delay. Increased protrusion of the coarse AP was observed using microscopic imaging of the surface. In the cited studies by Chakravarthy et al. and Bilerger et al., the course AP was able to extend past the surface enough that the heat from the gas phase could allow it to burst on the surface.

During the course of the PLIF study the authors noted that the diffusion flame height tended to increase with the propellant burning rate. The BDP model proposed by Beckstead et al. [3] dictates that the diffusion flame height above an AP particle is given by:

\[ X_d \propto \frac{\rho_c r_b R d^2}{D_o T^{0.75}} \]  \hspace{1cm} (2.14)

where \( \rho_c \) is the density of the propellant, \( r_b \) is the linear burning rate, \( R \) is the gas constant, \( d \) is the AP crystal diameter, \( D_o \) is the species diffusion coefficient, and \( T \) is the AP surface temperature. To eliminate diameter dependence from Eq. 2.14, the authors measured diffusion flame height from
particles in the 300-400 $\mu$m range. The diffusion constant $D_0$ and the surface temperature $T$ should remain constant regardless of the formulations, making the diffusion flame height proportional to the linear burning rate, $r_b$. The authors go on to note that the TMO catalysts used did not cause longer diffusion flame heights directly, but rather increased the burning rate, indirectly causing an increase in flame height. They state that the use of TMO catalysts in propellants increases the mass burning rate, which causes the diffusion flame envelope to go further into the gas phase.

The effect of the catalyst on the gas phase above the fine AP/binder was measured by comparing relative OH concentrations of Propellants. The images captured using the PLIF system were analyzed in the region above the fine AP/binder only. Vertical OH intensity profiles were analyzed starting just above the surface and extending 2.5 mm into the gas phase.

Titanium Dioxide Catalysts

Many of the previously mentioned metal-oxide catalysts have a well-documented catalytic basis, and follow typical trends of catalysis by lowering activation energy of the decomposition reactions directly, or altering the enthalpy of reaction. Titanium dioxide, by contrast can have a catalytic effect which more typically acts on the gas phase reactants, thus altering the gaseous conditions, and acting upon the AP crystals indirectly. It is for this reason, that titanium dioxide, commonly known as titania, was picked as a material of interest for the present catalytic study. Titania exhibits primarily three phases, rutile, anatase, and brookite, but is mostly found in nature in its equilibrium rutile phase[26]. Titania is used as a source for titanium metal, as well as in its ceramic form for various photoactive and catalytic uses. As it is relatively abundant in the crust of the earth, it is most often obtained by mining it from ilmenite, or rutile ore and then thermochemically processing it. Bulk rutile typically has a brownish red color, but finely powdered rutile is a very pure white material, as is thus used as white pigment for paints and dyes. Furthermore, titania is
generally transparent in the visible spectrum, but very absorbent in the ultraviolet spectrum, and has thus been used as a transmitted radiation reducing agent in sunscreens, as well as coatings on UV-degradable materials such as polymers\cite{69}. The meta-stable phase, anatase, has garnered a high level of interest and research in recent years due to its unique properties in a wide variety of applications and uses in catalysis and photoactivity\cite{57}. Anatase powders and nanomaterials are relatively easy to synthesize via wet chemical syntheses, and easily scale up\cite{12}. It has shown applications in organic matter decomposition\cite{33}, hydrogen generation\cite{68}\cite{27}\cite{36}, solar energy\cite{9}, nitrogen fixation as well as many other electro-chemical, environmental, and biomedical applications. Anatase is also resistant to photodegradation, and is generally environmentally inert\cite{63}. Structurally, anatase is similar to rutile in that it also has a tetragonal unit cell, however it has a different space group, lattice parameter, density, and different elements of symmetry\cite{58}. These differences in the lattice patterning lead to a varied and interesting set of properties. Anatase also yields a white material with transparency in the visible spectrum, but blocks most of the UV spectrum. Anatase is only meta-stable in lower temperature conditions, and is found in ilmenite ore, or is often formed from the decomposition of a titaniaum alkoxide, titanium sulfide, or titanium halide precursors, such as titanium tetrachloride, or titanium tetraisopropoxide\cite{35}. Its lattice provides an efficient energy transfer matrix for electronic propagation and orbital transitions, leading to a lot of catalytic, and photocatalytic properties that can be tailoring by altering the morphology, size, impurity level, defect concentration, and configuration\cite{48}\cite{47}.

\textit{Crystal Structure}

Though rutile and anatase have different densities, both phases have tetragonal crystal structures. Rutile has a body centered tetragonal configuration of the titanium atoms in a P42/mnm\textsuperscript{15} space group with oxygen atoms occupying voids in the lattice. The eight corner titanium atoms are shared among eight other primitive cells, while the body centered titanium atom is fully attributed
to the unit cell. Four of the oxygen atoms are shared among two cells, while two of the oxygens are fully contained within the unit cell, leading to 6 total atoms in the cell, 2 titanium and 4 oxygen. Anatase has a tetragonal crystal, but with a more complicated, non-symmetric I41/amd15 space group shown below. The anatase unit cell contains 12 total atoms, 4 titanium and 8 oxygen, twice as much as rutile. However, the anatase lattice is more than twice the volume at: 136.30 Å compared to rutiles 62.434 Å\[57\]. This difference in theoretical atomic density manifests itself in a variety of mechanical properties. Anatase has both a lower specific gravity (3.9 vs 4.2) and a lower possible hardness (6 vs 6.5 Mohs).

![Crystal Structure](image1)

**Figure 2.4:** Crystal structure of (a) meta-stable anatase TiO$_2$ (b) equilibrium rutile phase

*Phase Diagram*

As shown in the phase diagram below, titanium and oxygen form a wide variety of complexes depending on the temperature and ratio of present species. For the current system, the tita-
nium/oxygen ratio of interest is 1:2, which only occupies a small portion of the temperature-composition chart. However, as mentioned before, this atomic ratio yields a wide range of kinetically stable phases.

As rutile is the equilibrium TiO$_2$ phase at STP, the transition from meta-stable anatase to rutile is an issue of kinetics. Therefore, a typical equilibrium phase diagram will not suffice without kinetic information. The phase diagram below shows a temperature-pressure phase diagram of bulk titania in an initial anatase phase, which is subsequently heated and pressurized for an hour. The phases in the equilibrium zones were determined using XRD data to determine phase presence. As can be seen, with increasing temperature and pressure the percent character of rutile increases until it is the singular phase. At even higher pressures, srilankite becomes present, and eventually becomes the single phase.
The figure above shows powder X-ray diffraction patterns of titania synthesized from two common precursors, titanium tetraisopropoxide, and titanium ethoxide. The XRD patterns give us interesting information about the relationship between the phases, and their manifested morphology. In general, any titania synthesis method will not yield complete character of a single discrete phase. The bulk material will be made up a finite percentage of rutile, anatase, and brookite, with different precursors and procedures yielding different energetically preferred percentages. Thus the phase diagram, though useful, does not give complete information about the structure, character, and properties of the resultant titania. Different precursors or the presence of contaminants can yield different surface conditions, thus altering or impeding phase growth and particle sintering. In the XRD spectra shown above, the degree of peak broadening can be seen to decrease with increasing temperature of heat treatment. Using the Scherrer formula, we can see that this corresponds to an increase in the crystallite size, as a result of grain combination in sintering. In the titania made with both precursors, we see that this crystallite growth occurs at or below 300°C. However, if dopants are added to the lattice, they can impede the formation of phase/grain growth up to high temper-
tures, with temperatures of 400°C or higher yielding the same XRD derived crystallite size[66].

\[
\tau \frac{K \lambda}{\beta \cos(\theta)}
\]  
(2.15)

**Nanostructures**

**Nano-spheres**

Nanospheres are some of the most common nanostructures found of titanium dioxide, as their properties can easily be tailored in facile one pot wet chemical syntheses. General synthesis occurs from the decomposition of titanium precursors, and can be doped, agglomerated, and dispersed in-situ to yield varying morphologies and properties based on the dopants, stabilizers, and phase growth inhibitors.

**Nanotubes**

Titania nanotubes and nanotube arrays have a wide range of uses due to their high exposed surface energy, and large aspect ratio. The nanotubes can be formed out of either predominately rutile, or anatase titania using a number of different methods. For individual nanotube synthesis, wet chemical routes can be used. As with many solvothermal processes for nanotube formation, colloidal nanoparticles are synthesized by reacting a titania precursor, such as titanium tetrachloride, with an oxidizing species. These nanoparticles are then placed in an autoclave, or similar pressure vessel to undergo pressured heating at around 110°C[63][34][11]. The higher pressure, and slightly elevated temperature produce conditions favorable for axial growth along a [010] direction, yielding a wrapped (100) plane[42]. This is a simple method for obtaining nanotubes, but due to the inherent randomness of the colloid, this process can only yield randomly oriented nanotubes in
either suspension or powdered form.

A method for generation of oriented bulk nanoarrays of titania nanotubes is that involving electrochemical anodic oxidation. The array begins as a sheet of titanium foil, as shown in figure which is generally submerged in an acidic electrolyte, and given a bias. The acid pits the surface of the metal foil until the pits form evenly spaced pores across the foil surface. In the pitting process, the outside of the pores are passivated to form titanium dioxide. The erosion process proceeds until deep passivated wells have been uniformly generated throughout the bulk of the foil. This process can be very useful for situations where preferential orientation is preferred, and can yield high incident surface area, while maintaining efficient charge conduction pathways to subsequent substrates[45].

Figure 2.7: Schematic process for anodic generation of titania nanotube arrays[45].
Titania Catalysts

Titania has been shown to be effective at oxidizing or reducing inorganic and organic contaminants in fluids, and has thus been the subject of a lot of photocatalytic research[58][24]. Titania acts as an advanced oxidative species under photon impingement through electron excitation and subsequent transport to reaction sites. Photons of sufficient energy $E=h\lambda$, will excite electrons into titania’s conduction band from its valence band, and leaves reduced charge sites known as holes. These electrons and holes can migrate to the titania surface, and act as reducing or oxidizing species. In addition to reducing or oxidizing contaminants from liquid phases, anatase and rutile to some extent possess the capability to catalyze gaseous material generation. Anatase has shown a great ability to split water molecules into resultant hydrogen and oxygen gas through photon generated electrons. Incident photons generate electron-hole pairs which then migrate to the surface, whereupon they provide the potential to reduce or oxidize the respective components in water to yield hydrogen and oxygen diatomic gasses[27]. This method, though inherently inefficient due to the low visible spectrum absorption from anatase titania, provides a cost effective, simple, sustainable method for producing hydrogen gas[23]. A very similar process is present for the conversion of carbon monoxide to carbon dioxide, where carbon monoxide adsorbs on the titania lattice and is supplied with electronic energy in the presence of oxygen, yielding a favorable conversion to CO$_2$, shown in Figure 2.8. This ability to catalyse solid species into gaseous reactants prompted the study of its use in decomposing ammonium perchlorate. As stated earlier, the rate at which the gaseous reactants are formed, and react with each other, can be a rate limiting step depending on the pressure and temperature of the decomposition region.
As previously stated, there is a large change in heterogenous catalysts’ effect based on their proximity to reaction cites, it can be highly desirable to verify the dispersion of catalysts in-situ. One novel application, which the author has investigated, is doping fluorescent lanthanides into anatase nanoparticles to induce luminescence in the titania material[12],[9],[46]. Figure 2.9 shows the band structure of Rutile and Anatase titania. Anatase titania has a matrix suitable for efficient energy transfer through the lattice, and between secondary species[53]. This allows for a high degree of tailoring of the titania band structures properties by way of doping, conjugation, and coordination. The method of luminescence in the present study is similar to the aforementioned excitation procedures, where UV and near-UV light can be used to excite electrons from titanias valence band, as well as europiums F orbitals into elevated states. These excited electrons can then
relax in a quantum fashion, or can scatter down through defect energy states, and subsequently fall with less energy. The combined effect of the titania, europium, and defect relaxation yields a red emission centered around 615nm.

![Figure 2.9: Band structure of Rutile and Anatase titania [58]](image)

Titania Nanoparticles Composites

Nanoparticle-polymer composites have shown a myriad of interesting mechanical[25], electrical[13], optical[43], thermal[15], and energetic properties[48]. The dispersion of the particles plays a major role in the manifestation of these properties[13][37]. Methods and metrics for determining the particle dispersion properties are therefore necessary for the practical use of nanoparticles in polymer-matrix composites. Common dispersion characterization methods include microscopic and spectroscopic inspection, impregnation of tracer materials, and flow modeling, each of which suffer from significant drawbacks. In the authors work on nanocomposite energetic materials, which consist of oxidizer crystals and nanoparticle catalysts dispersed in a polymer binder, the nanoparticle dispersion has a dramatic effect on the composite burning rate, but no convenient method exists to measure the dispersion properties without disrupting the catalytic effect of the nanoparticles. Quality control techniques have been proposed to use free interface capturing mod-
els as well as x-ray based measurement techniques[52]. The complex flow parameters of the granular paste and the number of different constituents in energetic composites make modeling a practical difficulty[49][41]. X-Ray, microscopic, and spectroscopic methods require sensitive equipment, are time consuming processes, and are limited to analyzing only small sections of the composite at a time. The authors recently demonstrated the use of optical/photographic methods to detect settling and segregation of fluorescing quantum dots in composite energetic materials;[50] however, performance-enhancing nanoparticles in energetic and other composites are generally not luminescent. Anatase titanium dioxide has been shown to be an effective catalyst for composite solid energetic systems [48][50][54][47][28] and provides an efficient energy transfer network for luminescence[14]. When doped with certain trivalent rare earth elements (Eu3+, Sm3+, Nd3+, Tb3+, Er3+), titania can exhibit significant, and sensitive luminescence[39]. These properties make it a suitable candidate for both heterogenous catalysis and dopant induced luminescence. In this paper, we present a general, facile, visible-light method for characterizing the dispersion properties of metal-oxide nanoparticles in a polymer matrix by doping with luminescent europium. In addition to detecting macroscopic settling and segregation, the luminescence intensity was found to be proportional to the nanoparticle agglomerate size. This method is therefore capable of rapid and simultaneous characterization of both macroscopic and micro/nanoscale dispersion properties of bulk nanoparticle-polymer composites. In the case of energetic composites, the performance-enhancing effects of the nanoparticles is shown to be undisturbed by the doping process.
CHAPTER 3: METHODOLOGY

Eu-TiO$_2$ Nanoparticle Synthesis

The TiO$_2$ nanoparticle catalysts were prepared using a hydrothermal synthesis from a titanium isopropoxide (TIP) precursor, and nitric acid stabilizer. In a roundbottom reaction vessel with an affixed reflux condenser, ethanol and deionized water were added in equal proportions, along with a small amount of 1N nitric acid, and were heated to its boiling point. Under aggressive stirring, TIP was added dropwise into the solution, where it started to precipitate. After four hours of reacting, europium nitrate pentahydrate was dissolved in a 50:50 ethanol/water mixture and added to the solution. The solution was allowed to reflux for 24 hours, after which the ethanol was distilled off, and the solution was subsequently neutralized, centrifuged, and washed with DI water. The washed nanoparticles were suspended in an 80:20 water:ethanol mixture, and were spray dried with a Bucci spray drier with an ultrasonic nozzle to form spherical agglomerates. The particle size of catalytic additives affects both the catalytic activity, and the mixing/settling behavior of the additive particles in the binder. As such, the proposed method can be used with the differing spray-drying parameters to create tracers that mimic the behavior of pure, catalytic additives of a wide range of sizes. In this experiment, two sizes of tracers were made to mimic pure additives of two different particle sizes, large (6$\mu$m) and small (3.5$\mu$m) particles. After collecting spray dried powder, the particles were either heat treated at 400$^\circ$C for 3 hours, or were used as is. These powders were used for some of the characterization (UV-Vis, photoluminescence, XRD, SEM), but to obtain truly representative characterization, the particles were dispersed in a common solid propellant binder, hydroxyl terminated polybutadiene (HTPB), and were mixed using the hand-mixing methods explained by Stephens et al. [54]. To mix the suspension into the HTPB, the concentration of the suspension was measured using thermogravimetric analysis. Upon determining the concentration,
the appropriate amount of suspension was added to a beaker containing HTPB stirring at 500 rpm at 50°C. Due to the insolubility of HTPB in water, the suspension tends to remain separated during the mixing process. As the mixture stirs under aggressive conditions, the particles become embedded in the polymer binder. The HTPB was cross-linked with isophorone diisocyanate (IPDI), and poured into \( \frac{1}{4} \) diameter strands of PTFE tubing to cure at 63°C. These strands were used for microscopy, burning studies, and optical inspection. To characterize the titania particles as accurate representations of the particles in the solid propellant, microscopic analysis was performed on the particles while embedded in the HTPB binder. To obtain sections of appropriate thickness for TEM, SEM, and confocal microscopy, an ultra-cryomicrotome with a diamond blade was used to generate sections ranging from 10nm to 15 \( \mu \)m. Sections were cut at -120°C to decrease the toughness and to allow the rubber binder to be easily cut. The lower temperature also promoted greater particle adhesion to the binder during cutting, decreasing particle pull out; when coupled with the ultra-sharp diamond knife, allows the agglomerate particles to be sectioned.

Illumination of the Embedded particles in a Rubber Binder

Sample strands were made using the different particle formulations, and with different mixing methods to evaluate if the particle fluorescence could be observed through the binder, and if qualitative information about the dispersion of the particles could be obtained using standard, inexpensive methods. A mercury arc lamp was used to generate light, which was subsequently smoothed with a convex lens and filtered with a 470-nm bandpass filter to generate blue light to illuminate the samples sufficiently and consistently. A Nikon D60 SLR camera with a red filter was used to image the illuminated strands, with an enclosure around the entire apparatus to prevent ambient light from affecting the imaging.
Bio-Conjugated Catalytic Nanoparticles

Solid state catalysis is a complex mechanism which can be drastically affected by catalyst size, morphology, surface condition, concentration, dispersal, and location to critical reaction sites. To better understand these mechanisms, as well as to tune solid catalysts to have the greatest specific effect, it is sometimes desired to arrange them into difficult to achieve, high free energy formulations. Hedman et al. have noted that catalytic additives tend to agglomerate at the interface of the AP and the binder, and that the catalytic effect is most pronounced at the fine-AP/binder
interface[20]. To effectively study the catalyst interactions at the AP surface, a conjugation technique was developed to coordinate the catalytic nanoparticles to the surface of the oxidizer microparticles. Normally, when the catalytic nanoparticles are mixed with the AP crystals, they agglomerate into clusters on the surface due to the preferential free energy configuration. To prevent this agglomeration, and test the effects of particle proximity to the AP surface, methods were developed to promote thin, uniform dispersions of nanoparticles on the 200 micron sized AP crystals. This project explores the possibility of using bio-conjugation to disperse nanoparticles into composite matrices for catalytic purposes. To overcome their natural characteristics, templating bio molecules can be used to arrange the particles into these difficult formulations to more completely understand the kinetics of the catalysis. Here we explore a novel method for biomolecule based nanoparticle conjugation with application to dispersion of catalytic particles in a solid matrix. These nanoparticle dispersions are coupled with different surface modifications and coatings to test out different catalytic properties, as well as to produce novel formulations. The effects of these various dispersions are then studied using microscopic, spectroscopic, and calorimetric methods.

One of the more prevalent methods of nanoparticle conjugation involves Watson-Crick base pairing. Watson-Crick base pairing is a method which uses single strands of DNA with a known nucleotide sequence coordinated to one of the species desired for templating, along with oligonucleotides coordinated to the other conjugated species. This method is advantageous due to the highly ordered arrangements that can be formed. However, the DNA loses its conjugation in high temperature, high pH or pOH, and aggressive solvents. Additionally, this method may not be suitable for conjugating many types of particles. Thus, it was desired to pick a bio-conjugation procedure which would produce a more robust coordination.

The bio-molecules selected for the conjugation were Protein A, and the Immunoglobulin G antibody. These molecules have one of the strongest affinities found in nature, and can hold their
bonds in the presence of more aggressive environments, once formed. Figure 3.2 shows the nature of the complex, and the binding sites of Protein A and an immunoglobulin structure.

![Figure 3.2: Binding sites of IgFC and Protein A (Obtained from http://www.tulane.edu/~biochem/med/1fc2_igg.gif)](image)

To perform the conjugation, titania nanoparticles from solution were coated with a silane coupling agent with an amine terminated silanizing molecule, 3-aminopropyltrimethoxysilane (APTMS). The APTMS molecule facilitates uses the primary amine (-NH$_3^-$) group to conjugate with the immunoglobulin protein, as it is positively charged, and outward facing, allowing for conjugation without denaturing of the protein. To coat the nanoparticles, APTMS was introduced into a TiO$_2$ solution suspended in toluene. The APTMS forms an O-Si-R bond with the hydroxyl groups on the TiO$_2$ surface.

At the same time, the AP crystals are coated with Protein A in a saturated solution of ammonium perchlorate to prevent additional dissolution. In later batches, AP particles were first coated with a
thin layer of cellulose acetate to fully preserve the particle morphology and crystallinity.

Once both components, TiO$_2$ and AP, are coated with their respective coordinating species, they are placed in a solution together to allow the IgG/Protein A complex to form, thus conjugating the titania nanoparticles to the AP surface.

To facilitate the crosslinking of the proteins at the binding site, a 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide crosslinking agent (EDC), was used in conjunction with N-Hydroxysulfosuccinimide (Sulfo-NHS). EDC, shown in Figure 3.3, is a zero-length crosslinker, meaning it causes conjugation of carboxylates to primary amines without joining the crosslinked product.

![Figure 3.3: (a)EDC molecule and (b) Sulfo-NHS molecule](image)

NHS, shown in Figure 3.3 is an ester which reacts with primary amines, yielding stable amide bonds, further increasing the coupling efficiency of the proteins. Sulfo-NHS behaves the same as other NHS esters, but it has a sulfonate (-SO$_3$) group on the NHS ring, which simply promotes water solubility.

The full bio-conjugation process, including the cellulose acetate coated AP option is shown in Figure 3.4.
Figure 3.4: Illustration of the Protein A/IgG conjugation procedure. Top, Titania nanoparticles are coated IgG. Middle, ammonium perchlorate is coated with Protein A. Bottom, polymer coated ammonium perchlorate is coated with Protein A. Right, Protein A coated ammonium perchlorate is conjugated with IgG TiO$_2$ nanoparticles.
CHAPTER 4: FINDINGS

Eu-TiO$_2$ Nanoparticle Polymer Composite

_Emission and Excitation Spectra_

The photoluminescence excitation and emission spectra of the Eu-TiO$_2$ agglomerate powders shown in Figure 4.1 closely match the standard orbital transitions expected from europium oxide. Areas of locally maximum absorption in photoluminescence spectroscopy correspond to excitation transitions and give corresponding emission spectra of the agglomerate particles, shown in Figure 4.1b.

These distinct absorption peaks corroborate the existence of excitation at 394 nm, 464 nm, and 534 nm and likely correspond to europium $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5D_1$, and $^7F_2 \rightarrow ^5D_0$ transitions, respectively[64][66][61]. There is also a broad excitation from the valence band to the conduction band in the titania host matrix, positioned around 386nm (3.2eV), which allows electrons to be excited in a broader range of UV light, and to subsequently relax through defect states into the elevated band of europium. As has been shown in numerous studies [31][12][53], Figure 4.1b shows that the particles have a sharp, narrow emission peak at 615 nm. This peak corresponds closely to an electronic transition from the 17374 cm$^{-1}$ state in the $^5D_0$ orbital to the 1036 cm$^{-1}$ state in the $^7F_2$ orbital of molecular europium. This single-molecule transition corresponds to a 612 nm emission, but when the transition occurs from an energy band in the solid state, the emission is typically shifted to a value of 615 nm[32][34]. This particular transition is amplified relative to the other orbital states through coordination, bonding, or complexion to host materials through lattice substitution, ligands, or other methods of bonding to secondary materials[46].
Figure 4.1: (a) Photoluminescence (PL) spectrum of the excitation frequencies of the EuTiO$_2$ and EuTiO$_2$-H samples with emission at 615nm. (b) PL spectrum of the emission frequencies with excitation at 464nm. (c) Schematic energy diagram of proposed possible electronic transitions in Eu-TiO$_2$ system.
The UV excitation, shown in Figure 4.2 at 394 nm was more intense than the near-UV peak at 464, but both caused emission in the visible red range at 615 nm. The heat-treated material, relative to the un-heat treated, had a greater intensity of absorption and emission at all peaks. This increase in luminescence after heat treatment is often seen in the fluorescence of lanthanide materials as a result of defect reduction, elimination of dangling bonds, and lattice strain reduction. These lattice modifications effectively increase the emission of fluorescent energy of lanthanides in host matrices, by increasing the efficiency of energy transfer to the emitting ions[18][29].
Variation of Spectral Intensity with Agglomerate Size

The nanoparticles of 3 different agglomerate sizes (90nm, 3μm, 10μm) were dispersed in HTPB, and the photoluminescence intensity of emission at 580nm and 615nm is plotted in Figure 4.3. Emission intensity at both wavelengths was found to increase with decreasing agglomerate size. The dependence of rare earth luminescence intensity with crystallite size has been profiled in several studies[40][55][67], but still remains debated as to the direct mechanisms[18]. For materials with dominant quantum confinement effects, there is a decrease in the luminescence with increasing particle size[18][55][51]. However, for materials with dominant defect interactions, the luminescence tends to increase with crystallite size[40][56]. This effect of the luminescence can be attributed to the reduction in grain boundaries, which generally act as quenching points for the luminescent energy. Whether these trends hold true for agglomerate size, as well as crystallite trends, depends on the material system, with varying literature results being presented[18][67][16]. However, holding a material system constant, trends in the luminescence with agglomeration condition can be resolved. Despite the inherent resolution limit of fluorescing light prohibiting optical resolution of ultra-fine nanostructures, the conditions of dispersion or agglomeration at the nanoscale can be connected to an overall change in the bulk luminescence. In the present system, increases in the agglomeration of the nanoparticles leads to decreased luminescence in the bulk composite. Additionally, we observed a shift in the relative intensity of the orbital transitions with varying polymer-embedded agglomerate size. As the agglomerate size decreases from micron to nano range, the $^5D_0^7 F_0$ transition at 580nm luminesces at a greater value relative to the 615nm transition intensity (for PL spectra, see Figure S3, SI). This relative peak intensity shift could provide another indication of nanoparticle agglomeration condition in the bulk polymer.
Figure 4.3: $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_0$ luminescence trend with agglomerate size of HTPB embedded Eu-TiO$_2$ particles, illuminated at 464nm. X-error bars represent the agglomerate size ranges; y-error bars are standard deviations of triplicate measurements.

**Crystallite Analysis**

X-ray diffraction (XRD) crystallite sizes Figure 4.4, indicates no change in crystallite size across the Eu-TiO$_2$ samples. Un-heat treated Eu-TiO$_2$ (EuTiO$_2$) powder shows a primarily anatase titania structure, with evidence of a (121) peak belonging to brookite near 30$^\circ$. Deconvolution shows that this (121) peak has slight a slight presence of (222) from europium oxide. However, after heat treating (EuTiO$_2$-H), the peak becomes dominated by the presence of (222) europium oxide. XRD of the non-doped TiO$_2$ powder (TiO$_2$) also exhibits the presence of a brookite (121) peak, which loses intensity after heat treatment (TiO$_2$-H).

The TEM micrograph shown in Figure 4.5a corroborates the XRD crystallite size calculations shown in 4.1, and reaffirms the assertion that the spherical nanoparticles that make up the varying agglomerate sizes are predominantly crystalline, and around 5nm in size. Selected area electron diffraction (SAED) (Figure 4.5b) of the agglomerated nanocrystals shows indexed diffraction rings consistent with the expected anatase crystal phase.
Figure 4.4: XRD patterns of pure and Eu-doped TiO$_2$, with and without heat-treatment.

Figure 4.5: (a) TEM micrograph of microtomed EuTiO$_2$-H sample shows the agglomerates are composed of 5nm spherical nanoparticles. (b) SAED analysis of the same sample confirms the anatase structure.

*Surface Chemistry of the Eu-doped Titania particles*

The spray-dried powders were analyzed by x-ray photoelectron spectroscopy (XPS) to study the surface elemental composition and chemistry of the samples with and without heat-treatment. The XPS spectra in Figure 4.6 show the surface chemistry of the fluorescing europium oxide in both the unmodified, and the heat treated states for the small and large agglomerates. The Ti 2P$_{3/2}$ peak
in the un-heat treated powder was positioned at BE=458.8eV, which is characteristic of the binding energy shift of Ti$^{4+}$ from 458.6eV, as a result of the formation of Ti-O-Eu bonds. However, the heat-treated samples showed a reduced Ti 2P$_{2/3}$ binding energy relative to the undoped powder, with a peak at 458.2 eV. The O 1s peak had two components at around 529.7 eV, and 530.8eV for both the heat treated and un-heat treated powders. These peaks would typically respectively denote surface oxide and hydroxide, however the 530.8 eV peak is likely also indicative of Eu-O surface bonds, shifted from the peak position of Ti-O bonds. As Eu$^{3+}$ and Ti$^{4+}$ have a large difference in ionic radius (0.0947 nm to 0.0605 nm, respectively, for six-fold coordination)[64], and thus a low solubility, it was originally hypothesized that the heat treating process would allow trapped europium to migrate to the surface of the nanoparticles, and form crystalline europium oxide in clusters on the surface, effectively increasing the presence of Europium at both the crystallite and particle surface. However, the surface chemistry data in Figure 4.6d shows a lower relative presence of europium to titanium after heat treatment, indicating that the Europium diffuses away from the surface of the titania. It should be noted that higher europium oxide surface content does not necessarily correspond to higher fluorescence intensity, as shown by the PL. Radiationless transfers of energy, or cross relaxation due to dopant pair formation can quench the fluorescence in materials with concentration of fluorescent molecules greater than the critical level, around 2 mol% for europium[34]. This quenching effect in materials in excess of the critical dopant level can be diminished if europium complexes are formed to reduce the vibrational coupling of hydroxide ions. This result can be achieved with organic ligands or covalent complexes that act as antennas to allow increased transmission of absorbed energy to the luminescent ions[59].
Figure 4.6: (a) Eu 3d2 XPS spectra. (b) Ti 2p3 XPS spectra. (c) O 1s XPS spectra. (d) Oxygen and dopant atomic ratios at the particle surfaces.

Particle Dispersion Monitoring

Microscopic Method

SEM microscopy was conducted to provide high-magnification images of the dispersed agglomerates within the polymer binder (Figures 4.7 b&c), which confirm they retain their spherical shape after mixing in the composite. Samples of the composite were also imaged using fluorescence confocal microscopy to confirm that the observed bulk luminescence of the composite originates from the individual nanoparticle agglomerates. The information gained about the particle dispersion and morphology by SEM is limited due to the small penetration depth into the rubber binder.
Figure 4.7: (a) Cured strand of HTPB binder with embedded Eu-TiO$_2$-H particles. (b) SEM micrograph of microtomed binder surface with embedded particles. (c) Particle individually sectioned in the binder. (d) YZ planar particle dispersion in the 3D confocal stack. (e) XY planar particle dispersion in the 3D confocal stack. (f) Illuminated bulk samples with corresponding digital image line intensity analysis of the catalytic agglomerates well-mixed into the binder. (g) Illuminated bulk samples with corresponding digital image line intensity analysis of the catalytic agglomerates poorly mixed into the binder.

By contrast, when confocal microscopy is used the particles embedded in the HTPB cross sections can be viewed through the whole sectioned sample. Thirty confocal images of the microtomed propellant cross section were taken, with focus at 0.5$\mu$m intervals ranging from the bottom to the top of the sample, and then assembled into a 3D stack to create a virtual representation of the particle dispersion. Laser Diodes at 405nm, 458nm, and 476nm were used to view the particles in their encasing rubber binder. This technique allows the particle dispersion throughout the entire 15$\mu$m microtomed section to be observed.
Visible Light Particle Monitoring Method

Based on the photoluminescence spectroscopy data, a visible-light illumination apparatus was developed consisting of a mercury arc lamp, blue and red wavelength band pass optical filters, and a DSLR camera, for photographic imaging of macro-scale composite samples containing the Eu-doped fluorescing nanoparticles. Fluorescence was induced in the particle-embedded HTPB strands according to the illumination setup (Figure 3.1). When the particles are properly mixed into the binder, shown in Figure 4.7f, it can be seen that the solid composite propellant strands with the Eu-doped particles exhibit significant, smooth luminescence under UV light. When the particles are intentionally poorly mixed into the binder, the samples show inconsistency, with areas of higher particle loading exhibiting greater luminescence, and areas of lower particle loading exhibiting lesser luminescence (Figure 4.7g). Color intensity line scans were performed across the sample, yielding the intensity profiles shown in Figures 4.7f and 4.7g. The intensity values under sample luminescence can be resolved using digital image processing to find areas at the surface of differing intensity, allowing for both a metric to characterize the nanoparticle dispersion. The areas of high particle loading show a red component value more than three times larger than the areas of low loading.

Catalytic Performance of the Eu-TiO$_2$ particles

Pure and Eu-doped TiO$_2$ nanoparticles were tested for use as catalysts in composite solid propellants. The samples for burning were prepared by mixing the spray-dried agglomerates with the HTPB binder using the aforementioned hand-mixing technique, and then mixing in monomodal-sized ammonium perchlorate (AP) crystals with an average size of 200µm. This produces a granular paste that was poured into the $\frac{1}{4}$” tubing to form strands consisting of 80% AP, 19.5% HTPB, and 0.5% of the nanoparticles. These strands were then burned in a high-pressure strand bomb
throughout the mid-level pressure range shown in Figure 4.8. The fitted lines of the burning rates correlation with pressure show that the burning rate of the strands containing the Eu-TiO$_2$ nanoparticles is nearly identical to the non-fluorescing, pure-TiO$_2$ particles, while both show profiles with a significant increase from the baseline, which contains no additive. This similarity in behavior shows that the Eu-TiO$_2$ maintains the significant increase in the burning rate provided by the pure-TiO$_2$ catalysts.

![Graphs showing burning rates](a)(b)

Figure 4.8: Burning rate results of both the (a) non-heat treated, and (b) heat treated catalytic powders. Both Eu-TiO$_2$ samples closely match the burning profile of their un-doped counterparts, with the fitted line of the heat treated powders being nearly identical.

Table 4.1: Dopant concentration, heat treating parameters, and resultant size of the various spray dried nanoparticles and nanoparticle agglomerates from the various samples

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Europium Content</th>
<th>Heat Treatment</th>
<th>Particle Size [nm]</th>
<th>Agglomerate Range [$\mu$m]</th>
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<tbody>
<tr>
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Bio-Conjugated Catalytic Nanoparticles

The success of the bio-templating of the catalytic TiO$_2$ nanoparticles was illustrated and demonstrated via numerous spectroscopic, and microscopic methods. Figure 4.9 shows an SEM micrograph of the 200$\mu$m commercial AP crystals used for the study.

![Figure 4.9: Close up view of commercial ammonium perchlorate particles](image)

AP crystals are highly soluble in water, so to perform the initial conjugation, the crystals were coated and conjugated in a fully saturated solution containing dissolved ammonium perchlorate.

Figure 4.10 shows an SEM micrograph of the result of the conjugation procedure. As can be seen, the crystals lost their spheroidal shape during the bio-conjugation, indicating that they partially dissolved and recrystallized during the procedure. However, the images, along with chemical analysis, showed that the conjugation was partially successful, and that patches of titania coating were present on the AP crystal surface.

To prevent the AP particles from dissolving during the conjugation process, the AP crystals were dip-coated with a thin layer of cellulose acetate, a polymer known to either increase the CSP burning rate, or keep it neutral[44]. Figure 4.11 shows an SEM micrograph of polymer coated AP.
Figure 4.10: The AP particles, after bio-conjugation. Particles are re-crystalized during the reaction process, and as such, show erratic morphology.

Figure 4.11: View of a cellulose acetate coated AP crystal.

Figure 4.12 shows a portion of an AP crystal where the polymer has been peeled back, while Figure 4.13 shows the accompanying EDX spectra of the polymer region, confirming the chemical nature of the cellulose acetate coating.

The cellulose acetate coating was found to greatly retain the shape of the original commercial AP crystals throughout the conjugation process. Additionally, coating efficiency was improved, as the binding sites were given a consistent substrate which was not at risk of recrystallizing, or destabilizing. Figure 4.14 shows the end result of the bio-conjugation utilizing the AP crystals that had been pre-coated with cellulose acetate.
As seen in Figure 4.14, there are significant regions of the AP particles which have a thin dispersion of titania nanoparticles. These nanoparticles are dispersed in a thin, nanoscaled layer, as opposed to large, micro-particulate clumps around the crystal surface. As Hedmen et al. noted, microparticles tend to agglomerate at the interface of the AP and the binder[20]. Using a templated method to place the nanoparticles at the crystal surface, insight should be gained as to the nature, and cause for the catalyst agglomeration, and if this phenomenon plays a crucial role in the decomposition process.
To assess the efficacy of the bio-conjugated nanoparticle catalyst, samples of material were analyzed thermogravimetrically using a differential scanning calorimeter. The bio-conjugated AP crystals showed a decreased enthalpy of reaction at the HTD compared to every other comparative formulation. No significant lowering of either the LTD or HTD was found when compared to the polymer coated AP, and the bio-conjugated coated was found to increase the HTD temperature by around 20°C. Based on prior studies, this would indicate that the bio-conjugated particles do not serve to catalyze the AP decomposition reaction, in either the LTD or HTD region. However, the decomposition region of the bio-conjugated AP crystals shows a narrowing of the exothermic peak, indicating that the material is decomposing over a narrower temperature range. Though this effect is mainly unmentioned in literature, the authors have noted that other propellant configurations, such as ammonium perchlorate recrystallized in the presence of iron doped tiania nanoparticles, have shown exothermic peak broadening at the same time as a heightened HTD decomposition temperature, shown in Figure 4.15. This particular propellant configuration demonstrated a significantly enhanced burning rate, relative to a baseline propellant, and such might indicate a correlation between peak narrowing and CSP burning rate. However, more work focused on strand...
burning of CSP would need to be done to investigate this correlation.

Figure 4.15: TGA/DSC decomposition profile of different AP-TiO$_2$ formulations
CHAPTER 5: CONCLUSION

The bio-conjugation procedure was demonstrated to be successful in producing a nanoscaled coating of solid state catalysts onto the AP crystal surface, without affecting the underlying crystal. However, little information can be gained about the effect of catalysts present at the crystal surface until samples can be incorporated into a full scale composite propellant, and the effect of the catalysts on burning rate and specific impulse can be measured. To improve the bio-templating procedure, it is recommended to use higher concentration of catalytic nanoparticles to facilitate a full surface coating of the AP particles. To achieve this, the quantities of both Protein A and the immunoglobulin G antibody would need to increase in proportion to the nanoparticle catalyst. Additionally, other silanizing agents, such as aminopropyltriethoxysilane (APTES), or other coating facilitation agents such as epichlorohydrine (EPH). By varying the polarity and solubility of the coupling agents, higher coating efficiencies could be achieved. Additionally, to gain a true understanding of the catalysts configuration on the CSP performance, a batch of titania coated AP large enough to be burnt in a strant burner would need to be produced, and compared to baseline values, as well as those of catalysts in other configurations.

Many methods can be taken to increase the decomposition speed of Ammonium Perchlorate, and increase the burning rate of the overall composite solid propellant. Numerous factors related to the AP size, shape, and morphology can be altered to tailor the reaction rate. However, one of the more tunable factors can be the inclusion of a catalyst to alter the rate of AP decomposition. Heterogenous catalysts can play an important role in decomposing the AP surface, and delivering reaction products to the CSP fuel. As seen during the course of the study, the solid state catalysis is highly sensitive to the dispersion and size of the catalysts, though many formulations of catalyst can be tuned to tailor the propellant performance. Through controlled templating, and dispersion of the catalytic nanoparticles, the performance of the CSP can be altered, and the relation between
catalyst and reactants can be studied. Additionally, by using dopants, we can track the quality of catalyst dispersion, giving facile insight to mixing and casting parameters, and allowing the nanoparticles to be tracked in a polymeric composite. Settling and agglomeration have shown visible light corollaries, allowing for fast measurement of the nano-catalyst conditions in-situ. By both tracking, and templating the catalysts into tailored configurations, additional insight can be gained into the highly complex AP decomposition reaction, and the nature of catalysis in a burning CSP environment.


