

# Visible-Light-Responsive Catalysts Using Quantum Dot-Modified TiO<sub>2</sub> for Air and Water Purification

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Photocatalysis, the oxidation or reduction of contaminants by light-activated catalysts, utilizing titanium dioxide (TiO<sub>2</sub>) as the catalytic substrate has been widely studied for trace contaminant control in both air and water applications. The interest in this process is due primarily to its low energy consumption and capacity for catalyst regeneration. Titanium dioxide requires ultraviolet light for activation due to its relatively large band gap energy of 3.2 eV. Traditionally, Hg-vapor fluorescent light sources are used in PCO reactors; however, the use of mercury precludes the use of this PCO technology in a spaceflight environment due to concerns over crew Hg exposure. The development of a visible-light-responsive (VLR) TiO<sub>2</sub>-based catalyst would eliminate the concerns over mercury contamination. Further, VLR development would allow for the use of ambient visible solar radiation or highly efficient LEDs, both of which would make PCO approaches more efficient, flexible, economical, and safe. Though VLR catalyst development has been an active area of research for the past two decades, there are few commercially available VLR catalysts. Those VLR catalysts that are commercially available do not have adequate catalytic activity, in the visible region, to make them competitive with those operating under UV irradiation. This study was initiated to develop more effective VLR catalysts through a novel method in which quantum dots (QD) consisting of narrow band gap semiconductors (e.g., CdS, CdSe, PbS, ZnSe, etc.) are coupled to TiO<sub>2</sub> via two preparation methods: 1) photodeposition and 2) mechanical alloying using a high-speed ball mill. A library of catalysts was developed and screened for gas and aqueous phase applications using ethanol and 4-chlorophenol as the target contaminants, respectively. Both target compounds are well studied in photocatalytic systems and served as model contaminants for this research. Synthesized catalysts were compared in terms of preparation method, nature of the quantum dots, and dosage of quantum dots.

## Nomenclature

4CP = 4-chlorophenol  
CEC = controlled environment chamber

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<i>eV</i>	=	electron volts
<i>GC-FID</i>	=	gas chromatograph-flame ionization detector
<i>LED</i>	=	light emitting diode
<i>PCO</i>	=	photocatalytic oxidation
<i>PDA</i>	=	photodiode array
<i>QD</i>	=	quantum dot
<i>rpm</i>	=	revolutions per minute
<i>TCC</i>	=	trace contaminant control
<i>UHPLC</i>	=	ultra high performance liquid chromatography
<i>UV</i>	=	ultraviolet
<i>VLR</i>	=	visible-light-responsive
<i>W</i>	=	watt
<i>XPS</i>	=	x-ray photoelectron spectroscopy

## I. Introduction

THE use of titanium dioxide as a photocatalyst has dominated the field of photocatalysis for several decades. Applications, both realized and forecasted, encompass a broad range of processes including hydrogen production via photocatalytic water splitting, chemical and biological purification of water and air, and synthesis of organic compounds. The most commonly used titanium dioxide is a commercially available mixture known as Degussa P25 and is a simple mixture of anatase (70-85%), rutile, and amorphous (minor) titania<sup>1</sup> and has demonstrated high PCO activity in numerous studies<sup>2-7</sup>. The anatase phase is known for its superior photocatalytic activity relative to the rutile phase<sup>8</sup> with a band gap energy of 3.2 eV. Based on this band gap, only photons with a wavelength of 388 nm or less (i.e. UV) have sufficient energy to activate anatase TiO<sub>2</sub><sup>9</sup>. Traditionally, Hg-vapor light sources are used in photocatalytic oxidation (PCO) reactors, but the presence of Hg precludes the use of these systems in crewed spaceflight environments due to the possibility of Hg contamination (i.e., bulb breaks). Ultraviolet LEDs are an emerging technology, and have proven to be a feasible excitation light source alternative. However, currently available UV-LEDs have low lighting efficiency (13%)<sup>6</sup>.

The high photonic energy requirements currently needed for effective TiO<sub>2</sub> PCO disallows effective use of indoor lighting or solar radiation, which only consists of ~4-6% UV radiation at the Earth's surface<sup>10</sup>, as energy sources. Furthermore, UV-activated photocatalysis using TiO<sub>2</sub> provides only a moderate reaction rate and somewhat low quantum yield due to a low electron transfer rate and high electron-hole recombination rate<sup>11</sup>. Thus, in its current state of development, TiO<sub>2</sub>-assisted photocatalysis is not feasible for high throughput processes.

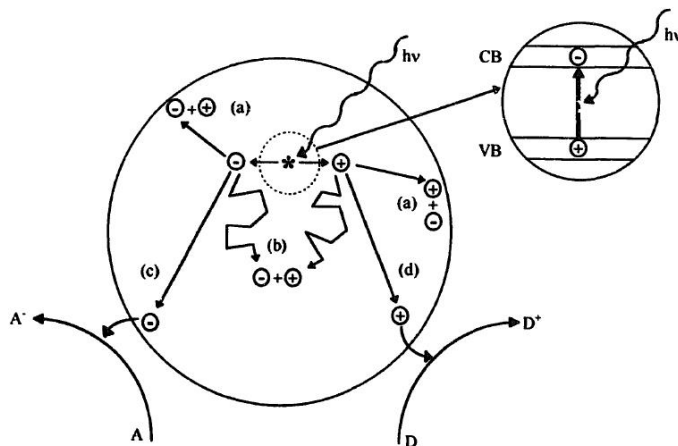
A solution for overcoming these limitations is to enable the TiO<sub>2</sub> photocatalyst to be activated by visible light. Developing a TiO<sub>2</sub>-based catalyst that is responsive to visible region wavelengths, will allow the use of visible band solar radiation (~45% of the solar spectrum lies in the visible region<sup>10</sup>), or highly efficient blue or white LEDs in PCO systems; thereby making PCO approaches more efficient, economical, and safe.

The development of Visible Light Responsive (VLR) PCO catalysts would facilitate the acceptance and incorporation of PCO-based technology for numerous ISS applications including use in air trace contaminant control (TCC) water recovery systems, low-cost hydrogen production using solar energy<sup>12</sup>, enhanced chemical and microbial purification of water<sup>13, 14</sup>; and potentially in the field of artificial photosynthesis. The past decade has witnessed a shift in catalyst development towards visible light responsiveness. Efforts have included sensitization of TiO<sub>2</sub> with absorbed dye molecules<sup>15, 16</sup>, metal cation<sup>17-21</sup> or anion<sup>22-24</sup> doping, narrow band gap semiconductor and TiO<sub>2</sub> coupling<sup>25-27</sup>, to name a few. Despite the vast amount of research in this field, conclusions regarding the relative effectiveness of any given method are difficult to draw due to the lack of consistent or standardized experimental conditions.

Beyond the necessity of a VLR photocatalyst to possess a narrow band gap capable of utilizing visible light photons (> 3.1 eV), it must also have suitable thermodynamic potential for the intended reactions and be resistant to photocorrosion. As seen in Figure 1<sup>28</sup>, the photocatalytic process begins with the absorption of a photon with energy equal to or greater than the band gap energy of the semiconductor, which causes the formation of an electron-hole pair. Most of the electron-hole pairs undergo recombination; however, a small percentage can move on to undergo oxidation or reduction reactions with adsorbed molecules. Redox potential relationships between the conduction and valence bands of the photocatalyst and target contaminant species (the species to either be oxidized or reduced) also play a crucial role in the success of this reaction. Specifically, the redox potential of a donor species (the molecules to be oxidized) adsorbed on the surface of the photocatalyst must be higher in energy than the valence band position of the semiconductor in order to replenish the electron vacancies and, similarly, acceptor molecules

(molecules to be reduced) must have a redox potential below the conduction band<sup>11</sup>. While narrow band gap semiconductors can use visible light photons to create electron-hole pairs, this redox potential requirement may not support effective breakdown of contaminants. Other considerations for possible photocatalyst candidates include their resistance to oxidation or reduction by water and their overall robustness under operating conditions (e.g., pH stability).

Several reviews on the current state of VLR-TiO<sub>2</sub> development have been published recently<sup>11, 29-31</sup>. Kumar and Devi<sup>29</sup> reviewed modified TiO<sub>2</sub> photocatalysis mechanisms with respect to interfacial charge carrier transfer dynamics; Zaleska<sup>31</sup> focused on metallic- and nonmetallic-doped TiO<sub>2</sub> preparation methods; Shon<sup>30</sup> discussed the effects of various ions and modification techniques in the attempt to create a VLR-TiO<sub>2</sub> catalyst; and Levine et al<sup>11</sup> related various modification techniques with photocatalytic activity and photonic efficiency. Further reviews are dedicated specifically to photocatalytic water splitting<sup>12, 32</sup>. All photocatalyst alteration methods have drawbacks. Dyes used as photosensitizers are slowly photodegraded, becoming less efficient over time<sup>33, 34</sup>. Metal-doped catalysts are often susceptible to thermal degradation or metal dopant molecules can serve as recombination centers rather than assist in the photocatalytic process<sup>20, 21</sup>. Coupled narrow band gap semiconductors can undergo photocorrosion with the possibility of releasing harmful side products. Drawbacks aside, many VLR catalysts have been successfully developed and further investigation of VLR-TiO<sub>2</sub>-based catalysts remains crucial to achieving high efficiency in such systems. This paper focuses on the development of a VLR catalyst library focused on coupling narrow band gap semiconductors with TiO<sub>2</sub> via two methods: 1) photodeposition, and 2) mechanical alloying. Further, the development of rapid screening assays for photocatalytic activity in both the aqueous and gas phases will be discussed.



**Figure 1: Processes occurring in a photocatalyst after electron-hole separation, including recombination of the electron and hole at the surface (a) and ion the bulk of the material (b), electron participation in the reduction reactions (c), and hole participation in oxidation reactions (d).**<sup>8</sup>

## II. Methods

### A. Light Source and Characterization

A custom light bank consisting of six 24-W Marine Glo T5 (60.96-cm length, 1.52-cm diameter) high output fluorescent bulbs from Hagen (Mansfield, MA) was designed as the light source for these studies. Irradiance profiles of the light bank at varied distances were determined in a dark room using a spectroradiometer (model OL754C, Optronics Laboratories, Orlando, FL). The light source was placed directly above the integrating sphere of the spectroradiometer at several heights (a 0.635-cm diameter light attenuating disc was used to avoid saturation of the detector during analysis). The height determined to have the highest irradiance was used to perform gas phase and aqueous phase assays described later.

### B. Catalyst Preparation and Commercial Catalysts

A total of 45 catalysts were prepared by two separate methods: photo-deposition and mechanical alloying for analysis. Prepared catalysts incorporated the use of metal sulfide quantum dots, metal selenide quantum dots, and/or pure metal with bare titanium dioxide. Degussa P25 TiO<sub>2</sub> (Evonik Industries, Essen, Germany) was used as the titanium dioxide source for all catalyst preparations and also as the traditional UV-activated photocatalyst for comparison. A commercial catalyst claiming high VLR activity, GENS NANO™ (Green Earth Nanoscience, Inc., Toronto, Ontario), was also compared to prepared catalysts. The VLR catalyst in GENS NANO™ is a proprietary, modified TiO<sub>2</sub> catalyst. Activation of the commercial catalyst is said to be possible with sunlight and everyday fluorescent lighting.

### 1. Photodeposition Method

Catalysts were prepared with metal or metal-sulfide quantum dots, following similar procedures. In a 125-ml Erlenmeyer flask, 0.25 g of Degussa P25 titanium dioxide and either 100 ml of 1:20 degassed ethanol:water or 100 ml of degassed water for quantum dot or pure metal deposition, respectively, was added. An appropriate amount of 0.1 M metal or sulfur stock solution was added to the flask to achieve 0.1 to 3.0% dopant loadings by weight. The flasks were placed on a stir plate approximately 3 cm from a 15W, T5 UV-A fluorescent bulb and allowed to react for 30 minutes (Figure 2). The flasks received a total of approximately 100 mW of UV radiation during the reaction. After the reaction completed, the catalysts were centrifuged to separate them from the liquid. The catalyst was then washed and centrifuged in deionized water three times before drying at 105°C overnight.



**Figure 2: Photodeposition preparation method for quantum dot formation on TiO<sub>2</sub>.**

### 2. Mechanical Alloying Method

Similar to the photodeposition method, catalysts were prepared with metal, metal-sulfide quantum dots, or metal-selenide quantum dots. In a 55-mL tungsten carbide milling vial, 1 gram of Degussa P25 titanium dioxide and either the dry material (metal or quantum dot) or 2 mL of toluene containing the material was added; two tungsten carbide balls were placed in the vial as the milling media. An appropriate amount of metal or quantum dot material was added to achieve 1.0-3.0 % dopant loadings by weight. The samples underwent alloying using a high-energy Spex SamplePrep 8000M Mixer/Mill (1060 cycles/min, 5.93 cm back-and-forth/2.54 cm side-to-side motion) for 5 minutes. Samples were placed under vacuum drying for one week.

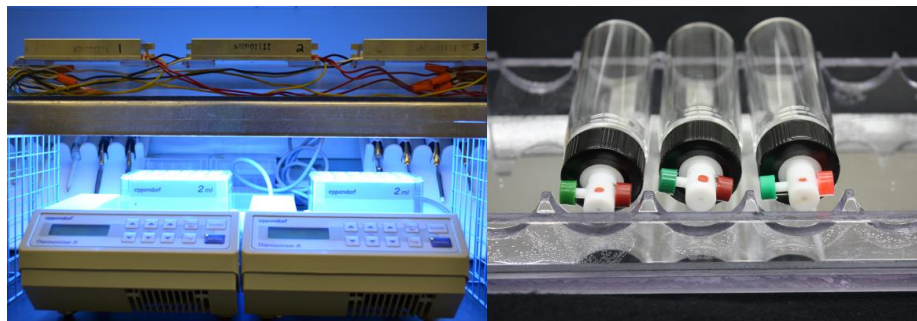
### C. Rapid Aqueous Phase Assay

For aqueous phase screening of VLR activity, 4-chlorophenol was selected as the target compound since it is a well-studied standard for photocatalytic oxidation. A catalyst loading rate of 10 mg/mL of contaminant solution was used. All reactions were performed in a Controlled-Environment Chamber (CEC) at 30°C; samples were allowed to adsorb the contaminant in the dark for 30 minutes followed by 30 minutes of visible light irradiation with stirring at 50 rpm (Figure 3). Analysis of the aqueous phase assay samples was completed using the Thermo Scientific Accela UHPLC (equipped with a Varian Polaris # C-18-A column, 100 x 2.00 mm) and photodiode array (PDA) detector. Evaluation of 4-chlorophenol removal was completed for all catalysts (degradation products were not identified in this rapid screening procedure). Removal of 4-chlorophenol (4CP) was calculated based the ratio of change in 4CP concentration to initial concentration (Equation 1).

$$\text{Removal \%} = \left( \frac{[4CP]_{\text{Initial}} - [4CP]_{\text{Final}}}{[4CP]_{\text{Initial}}} \right) * 100 \quad (1)$$

### D. Rapid Gas Phase Assay

The rapid gas phase screening methodology utilized ethanol as the target contaminant based on its well documented PCO mechanism. An aqueous slurry of the catalyst (5 mg/mL) was prepared and deposited onto aluminum coupons followed by evaporation to leave a thin film of catalyst. The aluminum coupons were placed in 40-mL, borosilicate vials outfitted with gas-tight septa lids for sampling (Figure 3). All gas phase reactions were completed in a CEC controlled to 30°C. The initial ethanol contaminant concentration was 50 ppmv to allow for sufficient detection of reaction products. Similar to the aqueous phase process, samples were allowed to dark adsorb for 60 minutes followed by 60 minutes of visible light irradiation. Samples were analyzed via an Agilent 6890 GC-FID equipped with an HP Plot Q column. The appearance of acetaldehyde, the main intermediate seen in the PCO of ethanol to CO<sub>2</sub>, was evaluated for VLR activity. This assay, designed to be rapid, was not optimized to allow for full mineralization of ethanol in the small, static vials.



**Figure 3: Aqueous (left) and gas (right) phase assays for rapid VLR activity determination of catalysts.**

## E. Catalyst Characterization

### 1. Diffuse Reflectance Analysis

Diffuse reflectance measurements were made using a Jasco V-670 UV/Vis spectrophotometer equipped with a 60-mm diameter integrating sphere. Catalysts were contained in a powder sample holder, which pressed the sample against a quartz window. Percent reflectance was measured between 300 and 800 nm at 2-nm intervals, referenced against a Spectralon certified reference standard (Labsphere, North Sutton, NH).

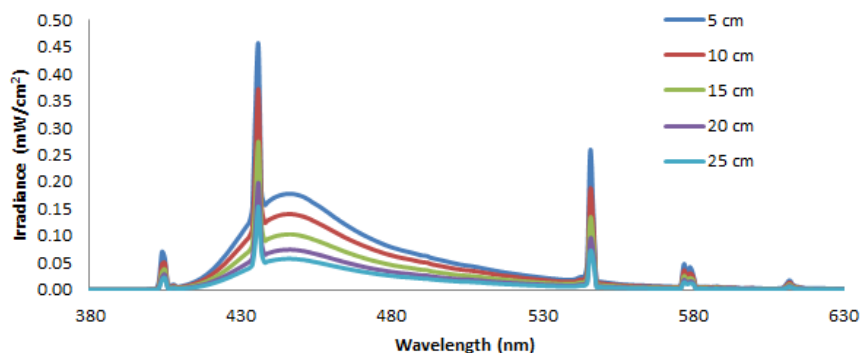
### 2. X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS analysis of catalyst samples showing appreciable VLR activity in either the gas phase or aqueous phase assays was completed on a Thermo Scientific K-Alpha system. Identical samples prepared via both methods outlined above were also compared to determine causes of differences in VLR activity.

## III. Results

### A. Light Source Characterization

Figure 4 shows the Marine Glo light bank irradiance profile and intensity at varied distances. The irradiance profile shows a broad peak ranging from ~400 to 500 nm due to the phosphor coating present on the wall of the bulb, while the sharp peaks in irradiance present at 404, 435, 546, and 578 nm are due to emission lines from the mercury contained in the lamps. Based on the emission spectrum, both the aqueous and gas phase assays were completed at a distance of 5 cm from the bulb to provide as much irradiance as possible to the photocatalytic reaction centers. Based on the distribution of wavelengths, a focus on quantum dots with absorption maxima of 480 nm or lower was implemented to best alter TiO<sub>2</sub> to be VLR.

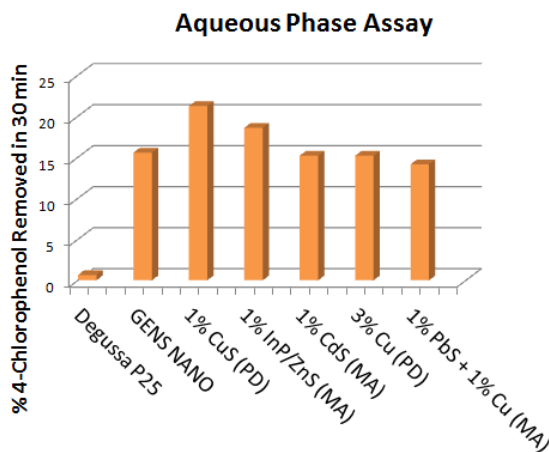


**Figure 4: Irradiance profile of Marine Glow light bank at varied distances.**

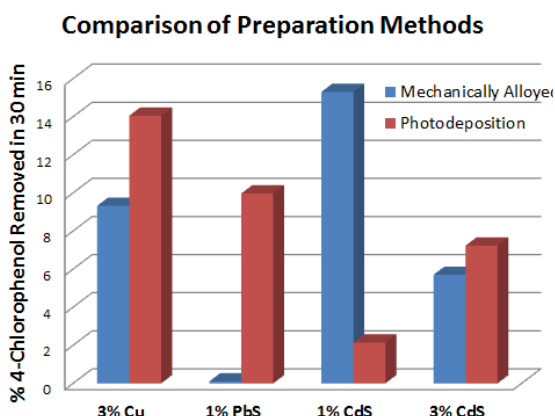
### B. Rapid Aqueous Phase Assay

Of the 45 catalysts prepared, five catalysts exhibited promising levels of 4-chlorophenol removal after 30 minutes of visible light exposure as seen in Figure 5 (0.4% destruction per minute or greater). Of the top-performing catalysts, two (1% CuS and 3% Cu) were prepared via the photodeposition method while the remaining

three (1% CdS, 1% InP/ZnS, and 1% PbS + 1% Cu) were prepared via the mechanical alloying method. It should also be noted that the Degussa P25 catalyst (control) had minute activity; this was likely due to the small amount of UV radiation emitted from the light source. The commercially-available catalyst, GENS NANO™, showed a 15.5% removal of the target compound after 30 minutes of exposure to visible irradiation and was outperformed (3% and 5.7% increase in removal after 30 minutes) by two of the catalysts prepared in house as shown in Figure 5, while the remaining three catalysts prepared in house exhibited near equivalent activity. This is a significant achievement and supports the need for continued research on these top performing catalysts. By refining these newly developed materials, it is likely that a catalyst with much higher activity than that seen in these initial studies can be obtained.



**Figure 5: 4CP removal capacity of top-performing catalysts in the aqueous phase assay compared to Degussa P25 (bare TiO<sub>2</sub>) and a commercially-available VLR catalyst (GENS NANO™). PD = photodeposition method; MA = mechanical alloying method.**

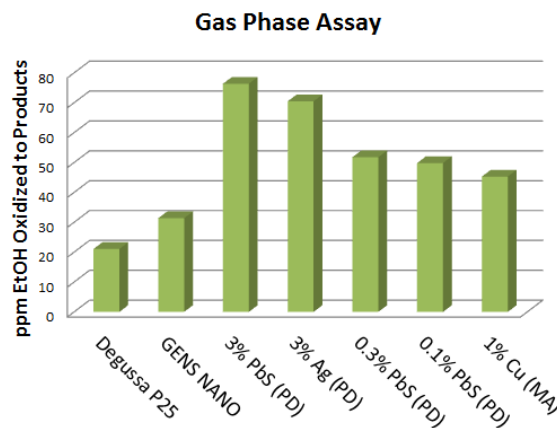


**Figure 6: Comparison of aqueous phase assay results with respect to comparison method.**

### C. Rapid Gas Phase Assay

Similar to the aqueous phase assay, the top five performing catalysts for the gas-phase photooxidation of ethanol are shown in Figure 7. The commercially available bare TiO<sub>2</sub>, Degussa P25, was found to have nearly 18% removal of ethanol after 30 minutes of visible light exposure, even with a polyacrylic UV filter in place. While the filter removed the majority of the UV radiation, it did not completely eliminate it; this minute amount of UV exposure is likely the cause for bare TiO<sub>2</sub> activity. Unlike aqueous phase photocatalysis where UV (and some visible) radiation is absorbed by water lowering the amount reaching the catalyst for activation, there are no UV hindrances in gas phase photocatalysis. Even the

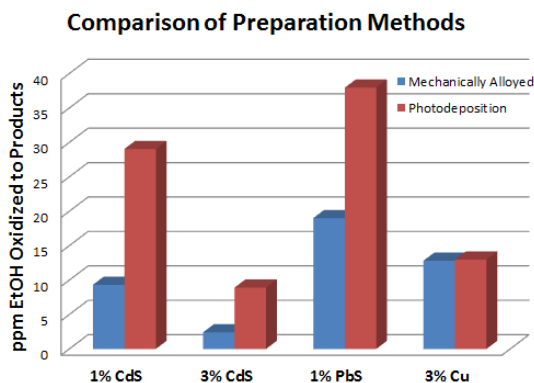
Neither preparation method proved to be more successful than the other in the current experiment (Figure 6); in some cases, the mechanical alloying method was observed to give higher VLR activity for the same type and dosage of dopant, while in other cases the photodeposition method prevailed. Further investigation into the relationship between the two preparation methods is warranted based on these results. If PCO activity between the two methods is determined to be equivalent for a particular catalyst, the mechanical alloying method would be favored, as it is the easier and faster technique. Furthermore, for catalysts prepared via the photodeposition method with high degradation performance, subsequent treatment of the mechanical alloying process could increase activity further by increasing the catalyst surface area. This was not tested during the project, but would be of interest in any subsequent work.



**Figure 7: Gas phase ethanol oxidation to products results for top-performing catalysts compared to Degussa P25 and GENS NANO™ catalysts. PD = photodeposition method; MA = mechanical alloying method.**

smallest amount of UV radiation passing through the filter will have an effect in the gas phase reaction.

The GENS NANO™ catalyst was seen to have a slight improvement of ~10% over the bare TiO<sub>2</sub> activity in the gas phase. It did not however reach activity levels near any of the catalyst samples prepared in-house, compared to results seen in the aqueous phase assay. These results show great promise for the quantum-dot modified catalysts developed during this study; however, further work is needed to fully characterize these catalysts. Figure 7 shows the results for the oxidation of ethanol to acetaldehyde (not a favored reaction product, as acetaldehyde is more harmful than ethanol). Constraints based on the reactor design, primarily the static vial system, limited the analytical techniques that could be employed thereby hindering full characterization and optimization of operating conditions. Future testing would involve the development of a more evolved reactor design to allow for a flow-through mode as well as optimized catalyst loading, contaminant loading, reaction time, etc. Optimally, the goal of photocatalytic oxidation is to fully mineralize contaminants (i.e., no intermediates/by-products); in the results presented, this was not achieved. However, the initial oxidation is still a worthwhile indicator of the catalyst efficacy; evolution of the reactor and test design will allow a more complete analysis.



**Figure 8: Comparison of gas phase assay results with respect to preparation method.**

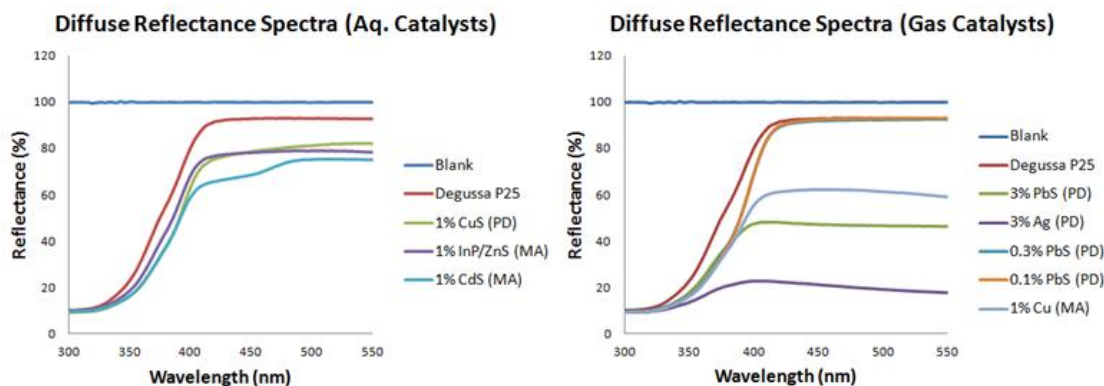
Unlike the aqueous phase results, a clear difference was seen in gas phase activity results depending on preparation methods. Here, the photodeposition method proved superior to mechanical alloying for all samples (Figure 8). The discrepancy between methods is likely due to oxidation of the metal and/or quantum dot species during the mechanical alloying process, a conjecture supported by XPS data (Section E), which showed definitive differences between metal and/or quantum dot peaks for the alternate preparation methods.

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## D. Catalyst Characterization

### 1. Diffuse Reflectance Results

Another method of studying altered TiO<sub>2</sub> for visible light activity is to study the diffuse reflectance spectrum of the material. Diffuse reflectance data allows for the calculation of a material's band gap energy, or the energy required to induce electron-hole separation. Beginning at high wavelengths in the visible region, the solid material should reflect a high percentage (up to 100%) of the light coming from the source. Once the band gap energy is reached, the material begins to absorb light, inducing electron excitation, and the reflectance decreases dramatically. This point is clearly distinguishable in diffuse reflectance data as a large change in slope in the reflectance spectrum (Figure 9). The point at which a line of best fit is tangent to the graph is the band gap energy requirement for the studied material.



**Figure 9: Diffuse reflectance spectra for top-performing catalysts.**

Compared to Degussa P25, if the spectrum of the new catalyst material experiences a red-shift in the reflectance shoulder (i.e., the spectrum is shifted to longer wavelengths), there will be a lower energy requirement for photocatalytic activity. In all the top-performing catalysts, the spectrum exhibited this shift and explains the

increased activity of the catalysts with the use of visible irradiation. As seen in Figure 9, several materials possess multiple shoulders in their reflectance spectrum. Degussa P25 appears to have two reflectance shoulders because its formulation contains both anatase and rutile forms of TiO<sub>2</sub> which possess slightly different band gaps. Other materials studied show multiple band gaps present due to TiO<sub>2</sub> and/or quantum dots or metals.

## 2. XPS Analysis

For those catalysts prepared using both preparation methods, x-ray photoelectron spectroscopy (XPS) was completed to study surface differences. In most cases, there were obvious differences between oxidation states of the metal and/or quantum dot species between the two methods. For instance, the definitive peak for lead in PbS was intact for the sample prepared by photodeposition but was altered in the mechanically alloyed sample (it is likely that the species was oxidized during the milling process, causing the lowered activity of the catalyst). The process of mechanical alloying, while useful for impregnation of dopants into compounds and for increasing surface area, has the drawback of high-energy and -temperature reactions. A compromise must be made between the advantage of surface area improvements and possible destruction of the catalyst during preparation. Again, further investigations with this method, both on its own and as a secondary treatment of photodeposition samples, can lead to a better understanding of valuable VLR catalyst preparation methods.

## IV. Conclusion

There has been an increasing amount of research focused on the modification of TiO<sub>2</sub> to render it visible-light-responsive. Despite the vast effort, conclusions regarding the relative effectiveness of any given method are difficult to draw due to the lack of consistent or standardized experimental conditions. This project as allowed for the development of successful rapid aqueous phase and gas phase assays to close this intellectual gap. Furthermore, an initial VLR catalyst library was built based on current and novel techniques for coupling TiO<sub>2</sub> with narrow-band-gap semiconductors. Several of the catalysts produced exhibited increased VLR activity over bare TiO<sub>2</sub> and over a commercially-available VLR catalyst, GENS NANO™. This project served to gather initial information on these top-performing catalysts including VLR activity and alterations in band gap energy and supports the need for further investigation into these materials. The evolution of this VLR catalyst technology will allow for its incorporation into many crucial ground-based applications as well as integration into existing ISS, and future space exploration, systems. Future work to further the knowledge gained from these studies includes a closer comparison of preparation methods for the top-performing catalysts, optimization of top-performing catalysts, and assays utilizing target compounds known to be more recalcitrant.

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