

Summer Scholar Report

Mechanistic Investigation of TiO₂ Photocatalysis

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Introduction

Water purification is a pressing issue around the globe, from California to India to Ghana. This project focuses on a method to create a water purification system that is off-grid and driven via sunlight using an economical and abundant material, titanium dioxide. TiO₂ is widely used as a white pigment, present in paint, toothpaste, sunscreen, candies, and more. The compound is also investigated by dozens of labs around the world, examining possible applications for splitting water, dye-sensitized solar cells, and photocatalysis. This report focuses on the photocatalytic properties of TiO₂ with the ultimate goal of using modified TiO₂ nanoparticles as a new method to decontaminate water.

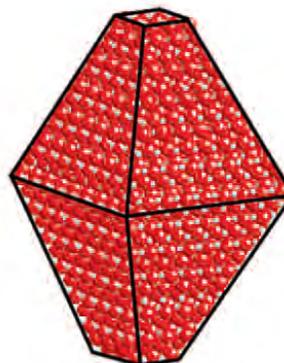


Figure 1. *Crystalline structure of an anatase TiO₂ particle.*

The scope of this project was to investigate the mechanism of ultranano TiO₂ photocatalysis. A greater understanding of the mechanism will allow for a more targeted approach to synthesis to create more efficient particles. Other groups have investigated four principle species in the TiO₂ photocatalysis mechanism: superoxide radical, hydroxyl radical, and the photogenerated electron and hole.¹ Many of the studies utilized Degussa P25, a commercial form of TiO₂. Degussa P25 is a mix of anatase, rutile and amorphous crystal forms across a distribution of sizes, with an average size of 20 – 25nm. The crystals studied in this project were consistently synthesized as anatase with a 2nm particle diameter (Figure 1).² The smaller size of these crystals indicated a significantly larger surface: bulk ratio. The makeup of Degussa P25 varies from batch to batch, with different ratios of crystal structures and morphological interfaces. The TiO₂ synthesized for this project was consistently reproducible 2nm anatase particles. These different properties were the motivation for an investigation into the mechanism of these specific particles.

Methods and Results

Ultranano TiO_2 was synthesized by adding 1.0mL of TiCl_4 dropwise to 300mL of deionized water at 0°C . After stirring for 40 minutes, the solution was dialyzed for two hours to raise the pH and grow the crystals to the appropriate size. The final step was to dry the solution using a rotary evaporator until solid white crystals remained. Adding 3.3mL of FeCl_3 to the reaction flask before adding the TiCl_4 created a more efficient TiO_2 nanoparticle with a stoichiometric ratio of one iron per every 200 TiO_2 units, thus called 0.5% Fe- TiO_2 , with a single Fe^{3+} per nanoparticle. Both types of synthesized particles were probed using UV/Vis spectroscopy to determine the particle size using the Brus equation (Figure 2).² The iron-doped and undoped particles were almost identical in size, approximately 2nm in diameter.

The efficiency of these particles was tested using a dual-arm photocatalysis cell. This reaction vessel had two 20mL samples loaded at once, allowing a direct comparison of the results. One side contained undoped TiO_2 and the other 0.5% Fe- TiO_2 , both with a 0.3125 g/L concentration. 0.2mL of methanol was added to each side, and a broadband Xenon lamp equipped with an IR filter irradiated the setup for 100 minutes, with aliquots taken at 10-minute intervals. The TiO_2 catalyzed the oxidation of methanol to formaldehyde. This product was reacted with O(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBOA) to form a complex that was analyzed by GCMS to determine the amount of formaldehyde obtained at each experimental interval. These results are shown in Figure 3. The ratios of the rates for the doped versus the undoped reaction show the relative efficiency of the modified particles.

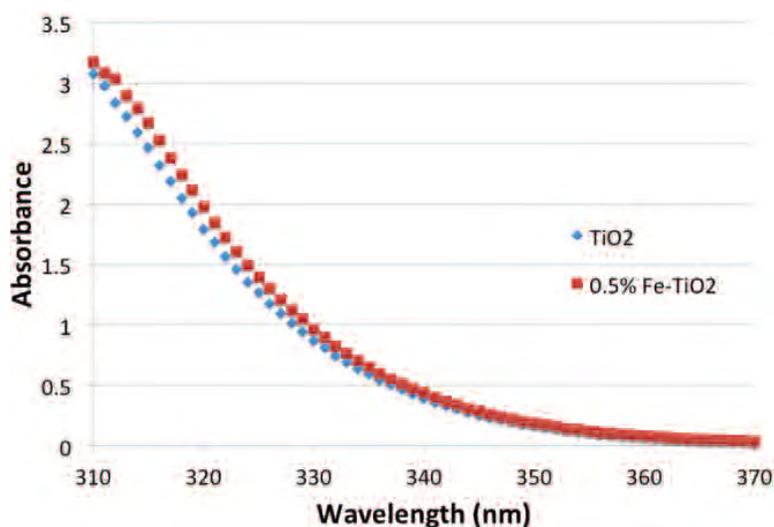


Figure 2. UV/Vis spectra of undoped TiO_2 and 0.5% Fe- TiO_2 . Data from these spectra were plugged into the Brus equation to calculate the particle diameters, both $\sim 2\text{nm}$.

Discussion

Titanium dioxide is a semiconductor with a band gap of 3.2 eV; this band gap is large, and thus TiO_2 usually requires UV photons to excite an electron.³ An overview of the photocatalysis mechanism follows. A UV photon is absorbed that excites an electron (e^-) to the conductance band, leaving behind a hole (h^+) in the valence band. If the e^-/h^+ pair recombines, the utility of that photon is lost. If the e^-/h^+ pair remains separated, the photogenerated electron reduces an electron acceptor and the hole oxidizes an electron donor, regenerating the catalyst. Many experimenters consider the electron acceptor to be molecular oxygen and the donor to be the molecule being oxidized (methanol in these experiments).⁴ The question that arises is: does TiO_2 photocatalysis occur via a heterogeneous or homogeneous mechanism? This question is important because TiO_2 has a low photoefficiency. Knowing the mechanism will facilitate targeting the slow steps to increase the viability of using TiO_2 as a photocatalyst for water purification.

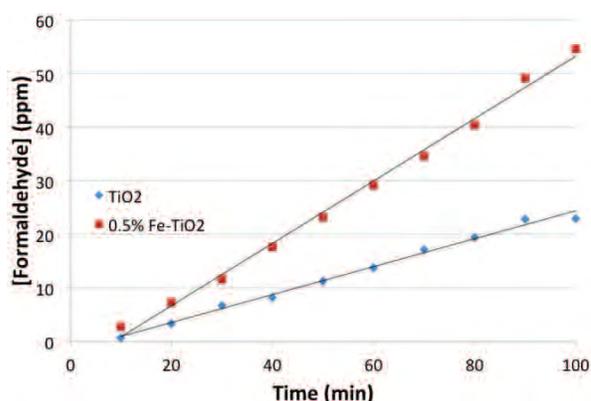


Figure 3. Plot of photocatalytic experiment with undoped TiO_2 and 0.5% Fe-TiO_2 showing formaldehyde concentration produced over the 100-minute experiment. 0.5% Fe-TiO_2 is 2.3 times as efficient as undoped TiO_2 .

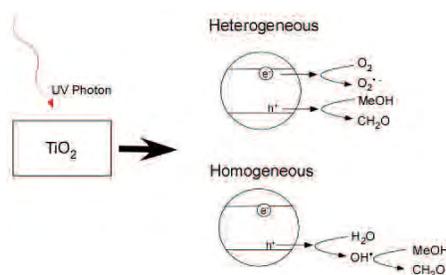


Figure 4. Heterogeneous and homogeneous reaction schema representing two possible mechanisms for the oxidation of methanol

A heterogeneous reaction occurs between two substances in different physical states, while a homogeneous reaction occurs between two substances in the same physical state. A hole on the surface of a TiO_2 nanoparticle directly oxidizing methanol to formaldehyde is an example of a heterogeneous reaction, as methanol is a dissolved liquid and TiO_2 is a solid suspended in water. If the hole oxidizes H_2O to hydroxyl radical ($\text{OH}\cdot$), this radical could oxidize methanol in solution as part of a homogeneous reaction. Both of these pathways may be possible (Figure 4). Direct oxidation by the hole should be the most efficient method, as a radical species could react with other molecules in solution rather than the target of oxidation. An investigation of these pathways can be performed using radical quenchers, specifically *tert*-butyl alcohol for the hydroxyl radical, *p*-benzoquinone for the superoxide radical, $\text{K}_2\text{S}_2\text{O}_8$ for the photogenerated electron and ammonium oxalate for the hole.⁵ The results for modified Degussa P25 in organic solvents indicate that the hydroxyl radical does not play a significant role in the mechanism and the other three species have varying levels of importance.^{1, 5} Given that the goal of this project is to use TiO_2 as a method for purifying water, identifying the important species in an aqueous system is crucial. These experiments are still ongoing for ultranano TiO_2 .

Non-aqueous solvents present another means to explore the mechanism. Hydroxyl radicals could easily be generated from the solvent in aqueous solution due to the large abundance of O—H bonds. In most organic solvents, the O—H bonds present are adsorbed OH groups on the TiO_2 surface and the alcohol that is added to the system to be oxidized to an aldehyde. Thus, investigating TiO_2 in an organic solvent using the same radical quenchers would allow for the role of water to be assessed in the mechanism. Acetonitrile was identified as a suitable solvent for these experiments due to its large dipole moment and ability to dissolve a wide range of substances. An issue arose when TiO_2 particles precipitated out of the solvent. The ultranano TiO_2 particles are so small that they form a transparent suspension in water, where they cannot be seen by the naked eye and do not scatter light. An organic solvent was required that would mimic water's ability to suspend the TiO_2 yet also be comparable to experiments performed in water. A key feature of these particles is their small size and large surface area; using a solvent that forces the particles to aggregate would not be comparable to results from the aqueous system. NaCl was used as a method to identify a suitable solvent, as the ultranano particles are comparable to a salt in that they are positively charged and coupled with an anion to form a crystal. Methanol was identified as the organic solvent that permitted the same TiO_2 concentration and particle size without scattering light. This system changed only one variable, the identity of the solvent, allowing all other components of the system to be directly comparable to the results from an aqueous system. A pilot study confirmed methanol as a suitable solvent. Figure 5 shows that formaldehyde was obtained linearly in time, confirming that this reaction was photon limited in methanol. This result enables further research into this area.

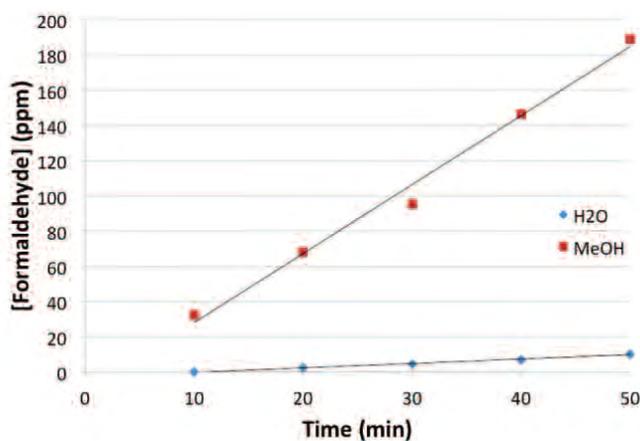


Figure 5. Plot of photocatalytic experiment using undoped TiO₂ in H₂O vs. methanol.

Conclusion

The photocatalysis mechanism of ultranano-titanium dioxide was investigated with the goal of applying knowledge of the mechanism towards improving the synthesis process. Heterogeneous and homogeneous pathways were discussed, creating a framework to analyze the data from radical quenching and solvent experiments. A deeper understanding of the mechanism is a crucial step towards building more efficient particles, with the ultimate goal of creating a solar-powered water purification system to address one of the greatest global health issues of our time.

References

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