**Quantification of Photon Flux of UV-LED Driven Photocatalysis**

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Submitted for PHY 481 in Partial Fulfillment of the Requirements for the Bachelor of Science in Physics

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May 2024

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# Abstract

The photocatalytic conversion of methane (CH4) to methanol (CH3OH) has gained the attention of many research groups in the last 10 years in the field of catalysis. Many reactions such as the conversion of methane to methanol are restricted by thermodynamic equilibrium and require extreme temperatures and pressures to be performed under thermocatalytic conditions. Photocatalysis proposes an alternative mechanism allowing for these reactions to be driven by light at standard temperature and pressure. The photocatalytic conversion of methane to methanol is motivated by its application to reduce the effect of methane on the environment, as methane is a potent greenhouse gas 20 times worse than CO2. Previous work in the field of photocatalysis has focused on studying and improving the efficiency of semiconductor photocatalysts such as titania (TiO2) that are employed in the photocatalytic conversion of methane to methanol. Contradictory experimental studies have reported that sulfur can enhance of decrease the photocatalytic activity of the photocatalyst. Though its overall role remains unclear, the modified activity could be related to the existence of sulfur-induced states in the band gap which extend the lifetime of electron-hole pairs. In this study, a constant current power supply compatible with a photon flux measuring integrating sphere was used to determine the photonic yield of two titania photocatalysts using a 385 nm UV-LED. Both photocatalysts show enhanced activity degrading methyl orange after being calcined to 450°C. The two catalysts denoted USR and NG, were measured to have an enhancement in the photocatalytic activity of 2.86 and 2.58 respectively after calcination. Although previous studies theorize that the enhanced activity is due to the narrowing of the band gap, as received and calcined samples displayed no discernable difference in their measured band gap suggesting that the enhanced activity is not due to the narrowing of the band gap, but rather the introduction of deep sulfur-induced electron traps in the titania structure. Methods of this project are developed using a batch photoreactor system to apply the designed UV-LEDs to a more complicated continuous stirred tank reactor capable of performing the conversion of methane to methanol reaction. By understanding the role of sulfur in titania, these improved catalysts can be applied to the conversion of methane to methanol and aid in the reduction of greenhouse gas pollution.

# Introduction

Global warming is defined as the average temperature increase of the Earth’s surface as caused by pollution from the accumulation of greenhouse gases in the atmosphere. Combat of global warming has become a priority of socio-economic policies due to its causation of heat-related and vector-borne illness, as well as decreased access to food and water. The global warming potential (GWP) is the measure of a greenhouse gas’s impact on global warming. In recent years, the greenhouse gas methane (GWP = 21) has doubled in production posing a greater threat to the sustainability of the atmosphere compared to the well-known greenhouse gas CO2 (GWP = 1)1 Prior research has estimated that 60% of methane pollution is from anthropogenic sources such as oil, coal mining, and mobile combustion that have led to a drastic increase in methane emissions between 1990 and 2010.1 Due to its existence in a gaseous state at room temperature, methane is difficult and costly to transport. As a result, methane produced at fracking sites is typically burned into CO2 to reduce greenhouse gas pollution by 20-fold. Not only does CO2 polluted by fracking contribute to environmental damage, but large underground methane transport pipes at these burn sites pose a threat to drinking water and wildlife populations due to their tendency to leak. These environmental concerns have led research groups to generate solutions to high methane pollution through photocatalytic conversion. Mainly research has focused on the photocatalytic conversion of methane to methanol due to methanol’s ability to be easily stored, transported, and used as a precursor to various chemical substituents. Recent progress in photocatalysis aims to develop a suitable method for converting gaseous methane into methanol driven by reactors and light sources that can be operated at fracking sites at a high percentage of conversion.2,3

From a chemical perspective, research in photocatalysis is motivated by its ability to run chemical reactions at mild conditions. Methane is a highly stable hydrocarbon due to its tetrahedral symmetry and heterolytic cleavage of each C-H bond requires a relatively large amount of energy of 432.373 kJ/mol.4 As a result, the conversion of methane to methanol via thermal catalysis is unfavorable unless under extreme pressures and temperature. However, the conversion of methane to methanol and many other thermodynamically unfavorable reactions can be achieved using photocatalysis at standard temperature and pressure using light energy. Titanium dioxide (TiO2) or titania is a semiconductor material that has been employed in the field of photocatalysis due to its ability to photodegrade organic pollutants and its accessibility from commercial manufactuers.5 Photocatalytic reactions using titania occur when a photon (light) excites an electron from the valence band to the conduction band, a process referred to as photoexcitation depicted in Figure 1. The valence band is the highest energy level fully occupied by electrons and the conduction band is the next available energy level which in the case of titania is empty. The gap between the valence and conduction band is called the band gap. A photon of energy greater than or equal to the band gap is necessary for this transition to occur. When an electron is excited to the conduction band it creates a vacancy or hole in the valence band that behaves as a positive charge due to the absence of the electron. The combination of the electron in the conduction band and the hole in the valence band is referred to as an electron-hole pair and can perform both oxidation (hole driven) and reduction (electron driven) reactions.

A diagram of a band diagram

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Figure 1. Photoexcitation of TiO2 semiconductor photocatalysts and successive photocatalytic reactions3

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The position of the valence and conduction band in the material directly influence the types of reactions that can be performed by the photocatalyst. The potential difference created by the electron-hole pair generate photoinduced reactive species in the photocatalytic reactions system as displayed in Figure 2. These reactive species are holes (h+), superoxide (.O2), and hydroxyl (.OH) radicals that are mainly involved in the degradation of organic pollutants.6

A diagram of a chemical reaction

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Figure 2. The valence band and conduction band positions of common photocatalysts2

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In addition, Figure 2 depicts the band gap of each material. The band gap is a property of the material and differs between photocatalysts based on their band structure and dopants. Titania, the photocatalyst of interest, has a band gap of 3.2 eV absorbing light in the UV region.7

Previous studies have investigated the role of dopants and their effect on the photocatalytic activity of titania.8 Most commercially available anatase contain sulfur as a dopant, the effect of which on photocatalytic activity has been studied by numerous groups.9,10,11 Contradictory experimental studies have reported that sulfur can enhance10,12,13 or decrease14,15,16 the photocatalytic activity by acting as electron or hole trap, although its overall role in photocatalysis remains unclear. The modified activity could be related to the existence of sulfur-induced states in the band gap. Empty trap states are proposed to scavenge electrons and promote charge separation, thereby increasing the lifetime of holes after electron-hole pair creation.17 Previous research to this project has investigated the effect of sulfur on the performance of photocatalysts. Although titania is used in the photocatalytic conversion of methane to methanol, experimental set-ups require the reaction to be operated under continuous flow conditions that create difficulty in evaluating the performance of the photocatalyst. Thus, both sulfur-doped and sulfur-free titania have been characterized previously by measuring the kinetics of the photodegradation of methyl orange in a batch reactor and extending upon the work of Bakar and Riberio.15

Recent literature suggests reporting the photonic yield to properly assess efficiency of the photocatalysts. The photonic yield is defined as the ratio of the rate of the photoreaction measured for a specified time interval (usually the initial conditions) to photonic yield incident photons of monochromatic light inside the irradiation window of the reactor as depicted in (1).18

(1)

To calculate the photonic yield, it is necessary to measure the photon flux of the light source used in the photocatalytic reaction. In this study the photon flux of a 385 nm UV-LED light source is measured and used to determine the photonic yields for previous photodegradation reactions for sulfur-doped titania photocatalysts to give quantitative data regarding the effect of sulfur on titania. Additionally, methods for designing a UV-LED lamp compatible with a continuous stirred-tank reactor are also explored to apply to both the photolysis of hydrogen peroxide and the photocatalytic conversion of methane to methanol to combat the effects of methane on the environment.

# Experimental Section

## Materials and Methods

The methyl orange (C14H14N3SO3Na, MW = 327 g/mol, maximum absorption wavelength = 466.6 nm) was purchased from Thermo Fisher Scientific. Commercially available sulfated-anatase catalysts were purchased from their respective manufacturers: Alfa Aesar (denoted “AA”, Lot. N05C073), Sigma Aldrich (denoted “SA”, Lot. MKCK5713), US Research Nanomaterials (denoted “USR”, Lot. US3490), Nanographi (denoted “NG”). Sulfate-free anatase was synthesized by Prof. Rachel Austin at Barnard College using sol-gel synthesis from TiCl4 (denoted “BC”)19 followingthe procedure outlined by Li et al.20 The system used to perform calcination and diffuse reflectance measurements is shown in Figure 2.1. Gases were fed to molecular sieve traps, containing molecular sieve (13X, 4-8 mesh), to rigorously remove water vapor. Traps were activated prior to use by heating to 200 °C under the flow of N2 for at least one day. Traps were cooled with ice water during operation. The design allowed for one to be activated while the other was being used over the course of the calcination. Gas lines were heat traced all the way to the calcination reactor and the environmental cell, excluding the mass flow controllers (MFC). The reactor consisted of a 0.5” diameter stainless “U-tube” steel tube placed in a rectangular oven heated with heat tapes installed with thermal paste. The oven temperature was controlled by an Omega ¼ DIN Ramp/Soak/Process temperature controller based on a K-type thermocouple in contact with the catalyst in the U-tube. The USR anatase, denoted as “USR 450”, was calcined by loading the sample (5.0 g) into the calcination reactor and increasing the temperature stepwise 100, 200, 300, 400, and 450 °C holding for a minimum of one day at each temperature under the flow of 100 sccm of O2 as controlled by an MFC. A low sulfur content sample, “SA 500” was prepared by Christian Geci. A sulfur-free sample, denoted “BC 400”, was prepared previously by Akbar Madahvi-Shakib by calcination for several days at 400 °C.

A diagram of a machine

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Figure 3. a) A schematic of the calcination setup, UV-Vis and praying mantis Harrick cell/environmental chamber, calcination reactor tube, and the dry gas lines of Ar, H2, N2 and O2; b) schematic of calcination U-tube reactor.

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A 1.49x10-3 M stock solution of methyl orange (250 mL) was prepared by diluting methyl orange (122.02 mg, 0.373 mmol) in a beaker of deionized water and quantitatively transferring to a volumetric flask (250 L). From the stock solution, 2.984x10-5 M methyl orange solutions for decomposition reactions were prepared by quantitatively transferring methyl orange (20.0 mL) and diluting in a volumetric flask (1.0000 L).

## Batch Photoreactor Design and Characterization

The experimental system used was constituted by the following components and were used to carry out photodegradation experiments (Fig 4A):

(i) A 5.18 W 385 nm LED Lamp was constructed by wiring two LEDs (Digikey: LZ1-10UBN0-00U5) in series and mounting the LEDs on opposite sides of the base of an aluminum rod (16.3 cm × 5 mm; length × thickness). A heat sink was mounted to the top of the aluminum rod (Digikey: 345-1126-ND, Pdiss = 11W). The lamp has a spectral energy distribution between 380 – 390 nm wavelength region (Fig 4B) and the intensity was varied with forward current between If = 100 – 500 mA (Fig 4C) to measure the intensity with a silicon diode using a homemade UV-Vis DRS system.17 (ii) An immersion well implemented with a Pyrex test tube (20 mm × 150 mm; diameter × length). (iii) A 50 mL plastic beaker containing a TiO2 slurry in methyl orange solution with a magnetic stir bar. (iv) A cardboard safety sleeve mounted on top of a stir plate to prevent exposure to the UV light. The magnetic stirrer was used to suspend the TiO2 in the slurry.

A diagram of electrical components

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Figure 4. A) LED Photoreactor set-up; B) Spectral energy distribution of 385 nm LED Lamp; C) Integrated area of UV-Vis Peak vs. Forward Current; D) Initial rate of degradation of 75µm AA vs. Forward Current.

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In addition, different LED light sources were employed to cover the wavelengths 390, 395, 410, and 455 nm. The integrated area was calculated from the UV-Vis peak and behaves linearly with forward current (Fig. 4C). These rates were measured at the optimal rate regime in which photon absorption is at a maximum. The photon flux of the LED behaves linearly with forward current as indicated by the linear increase in initial rate of 75µm AA (Fig. 4D). The rate vs. forward current measurements were made using 40.1 mg of AA in 80.0 mL of methyl orange solution.

## Continuous Stirred-Tank Photoreactor and LED Lamp Design

A UV-LED lamp compatible with an assembled Ace Glass continuous stirred-tank reactor (CSTR) was designed and depicted in Figure 5. The UV-LED lamp provides several advantages over a Mercury-Vapor lamp; 1) the CSTR can be ran at smaller volume and the amount of 30% hydrogen peroxide being pumped to maintain steady state can be reduced; 2) the smaller volume prevents methane gas from bubbling and entraining lines of the GC-MS used for analysis; 3) the UV-LEDs dissipate little heat in comparison to the Mercury-Vapor lamp making the need for cooling water lines obsolete.

Diagram of a diagram of a water heater

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Figure 5. Designed Photoreactor and LED Lamp

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## Constant Current Power Supply Design

A 12V DC power supply was ordered from Digikey that can power the two UV-LED lamp design (Vmin = 7.4V). Wired connections were made to the live (black), neutral (white), and ground (green) components of the power supply to allow it to be plugged into the 120V wall socket (Figure 6).

A collage of a computer and a machine

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Figure 6. A) Power supply before connections and B) after connection were made

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The 120V wall socket was measured with a multimeter to determine the live, neutral, and ground components of the socket and cross-checked to ensure compatibility with that of the power supply’s plug. The next step of engineering the power supply was to design the “constant current” component. The idea for the design of this circuit was to choose the simplest circuit possible. The idea of using various diode and transistor circuits was considered, but eventually a circuit element known as an LM317 was chosen due to the complexity of these transistor circuits. The LM317 is an adjustable positive linear voltage regular that can be operated using an input voltage between 3 – 40 V, but will always deliver an output voltage of Vout = 1.2 ± 0.05 V. The LM317 has an input, output, and adjust terminal; the adjust terminal ensures the output terminal voltage is always 1.2 V higher. Using the properties of the LM317 a functional constant current circuit powered by the 12V power supply was developed as illustrated in Figure 7.

A diagram of a circuit

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Figure 7. LM317 Circuit Diagram

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The limited current (Ilim) of this circuit can be controlled by the adjustable resistor of this circuit described by Equation 2.

(2)

The standard current for running photocatalytic reactions with UV-LEDs is 500mA, therefore the necessary resistance of the adjustable resistor (Ωmax = 5 Ω) should be 2.4 Ω for these experiments. Unfortunately, there are two constraints to the simple LM317 power supply design; 1) the chosen power supply voltage output limits the number of LEDs on the lamps to three LEDs (Vmax = 11.1 V) and 2) the simple LM317 circuit does not allow for the measurement of the photon flux dependence of photocatalytic reactions without taking apart the power supply. To work around the second constraint, a second LM317 circuit (denoted S-LM317) was designed to allow the operator to switch between high current (R1 = 2.5 Ω, 500 mA) and low current (R2 = 5 Ω, 250 mA) paths to measure photocatalytic reactions at different photon fluxes (Figure 8).

A diagram of a circuit

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Figure 8. S-LM317 Circuit Diagram

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Both the LM317 and S-LM317 circuits were constructed in the final design of the constant current power supply in Figure 9. The final power supply contains two terminals; the first operates the power supply at a constant current of 500 mA, and the second operates the power supply at either 250 mA or 500 mA depending on the user’s selection.

A machine with wires and wires

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Figure 9. Final Power Supply

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## Photodecomposition Reaction

Photodegradation experiments were carried out with the LED Photoreactor set-up represented in Fig. 4. The photodegradation experiments were conducted in a batch reactor set-up. For the UV LED experiments, 40.0 mL of methyl orange solution and the specified mass of catalyst was used. An aqueous solution was prepared by 2.98x10-5 M concentration of methyl orange adjusted to neutral pH with 0.1 M NaOH as necessary. A pH meter (VWR Scientific Products model 2100 pH/Temp/mV meter) was used for pH measurements. The concentration of methyl orange was determined using a Vernier UV-vis spectrometer. To determine the concentration of methyl orange, three 2.0 mL samples were taken at preselected time intervals (0, 5, 15, 35, 75, 115 minutes), centrifuged, and recombined into the reaction mixture after analysis. Catalysts were determined to be sufficiently separated in the centrifuge when the baseline in the 600 nm region of the UV-Vis returned to a similar absorbance as recorded for the stock solution. Samples were measured in triplicates and the error was plotted using the least mean square method. The concentration of methyl orange was calculated from the absorbance at the wavelength of 466.6 nm by using a calibration curve made by Batoosingh,21 who determined the molar absorptivity: 25701 cm-1M-1.

## UV-Vis of Band Gap Measurements

UV-Vis diffuse reflectance spectroscopy (DRS) band gap measurements of photocatalysts were done with a home-made UV-vis DRS system. The UV-vis excitation source was a 75 W Xe lamp (Edmund Scientific) and dispersed in a scanning Czerny-Turner monochromator (HORIBA Scientific Production, IBC) accessory. The instrument was equipped with a Praying Mantis (Harrick Scientific, IBC) accessory for DRIFTS applications and the reflected light from the sample surface was detected with a silicon detector (Edmund Scientific). The detector output was amplified by a low-noise amplifier (model 181, Princeton Applied Research) and averaged with a digital multimeter (Keithley 2000, Keithley Instruments) with a computer interface.17 The UV-Vis signal was aligned to read a signal of 8 V at 467 nm. The TiO2 samples were diluted to 5% in KBr by rigorously grinding KBr and TiO2 together for five minutes. KBr background spectra were measured in triplicates and samples were removed carefully to not disrupt the alignment. The diluted samples were loaded into a sample cup for spectroscopic measurements. Measured spectra were transformed into Kubelka-Munk units and extrapolated using the Tauc Plot method to determine the band gap following the procedure outlined by Makula *et al*.7

## Integrating Sphere Photon Flux Measurements

Calibration of the 385 nm UV-LEDs was carried out using a Thorlabs PM100D optical power meter with a S-120Z filter for relative power measurements ranging from 10 – 500 mA reported in Figure 10. The UV-LED shows a linear relationship to power. The integrating sphere was calibrated with a LS-1-Cal calibration light source with an 8036 ms integration time. Photon flux measurements were made with an ocean optics integrating sphere and operation current of the UV-LEDs at 10mA.

A graph of a calibration curve

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Figure 10. Relative power calibration curve for 385 nm UV-LED

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# Results

## Kinetics of Methyl Orange Degradation: USR and NG

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Figure 11. Mass Dependence of Photocatalysts Illuminated by 385 nm LED Lamp

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Figure 11 depicts the photocatalytic rate of methyl orange degradation as a function of catalyst mass as illuminated by a 385 nm UV-LED lamp operating at If = 500 mA. Both the USR AR and USR 450 exhibit similar behavior: at low catalyst masses, the degradation rate increases linearly while at higher masses the rate reaches a maximum and plateaus to a rate referred to as the optimal rate.18 At low mass or differential conditions, the rate varies between catalysts due to factors such as scattering effects, the absorption coefficient, and the degree of suspension in solution. Under these conditions, it is not possible to accurately determine the amount of light absorbed and thus assessing photocatalytic efficiency is difficult. To properly compare the photocatalytic performance between photocatalysts, the reaction rate must be evaluated under conditions in which the photon absorption and rate are maximized. If the photon flux of the light source can be measured, the photocatalysts can be compared based on their photonic yield. For the NG AR catalyst, data points were collected at masses of 25 and 30 mg, however, it remains unclear whether these are measured in the optimal rate regime. The NG 450 sample exhibits a linear mass dependence from 5 to 20 mg followed by a significant increase in rate at 25 and 30 mg in the optimal rate regime.

## Determination of Photon Flux and Methyl Orange Photonic Yield

The photon flux of the 385 nm UV-LED was determined by measuring the total photons at 385 nm over an integration time of 8036 ms at 10 mA. The photon flux was calculated as follows:

A graph of a graph showing a line of led

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Figure 12. Photon Flux Calibration Curve for 385 nm UV-LED

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The photon flux measurement at 10 mA was used with the relative power calibration curve (Figure 5) to create a photon flux calibration curve. The photon flux calibration curve illustrated in Figure 12 was used to calculate the photon flux at the current in which the methyl orange degradation kinetics measurements are made (photon flux (500 mA) = 1.81 \* 1016 photons/s). The photonic yield is calculated for USR 450 utilizing Equation 1 as follows:

(1)

\*Note: The rate in the optimal rate regime must be converted to methyl orange atoms / min.22

\* 100

114%

Table 1. Optimal Rate and Photonic Yield of USR and NG Catalysts

|  |  |  |
| --- | --- | --- |
| Catalyst | Optimal Rate (M/min) | Photonic Yield |
| USR AR | 3.96 \* 10-7 | 39.9 % |
| USR 450 | 1.13 \* 10-6 | 114 % |
| NG AR | 3.57 \* 10-7 | 36.0 % |
| NG 450 | 9.23 \* 10-7 | 93.0 % |

There is an issue with the photonic yield measurements made. The photonic yield should not exceed 100% as it is does for USR 450. This is most likely due to two experimental constraints; 1) the 385 nm UV-LED is wired in a way that the entirety of the LED cannot be inserted into the integrating sphere; 2) the UV-LED has a distribution of wavelengths above the band gap that also contribute to the reactions aside from 385 nm. Thus to measure a more physically reasonable photonic yield the photon flux of each wavelength above the band gap of the photocatalyst must be measured. Additionally, modifications to the LED wiring or integrating sphere set-up must be made to ensure all photons are measured by the detector.

## Band Gap Measurements

A graph of different types of energy

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Figure 13. Top) Absorption Spectra Plotted in Kubelka-Munk Units and Bottom) Tauc Plots

To estimate the band gap energy by UV-Vis DRS, 0.5% by weight of USR AR and USR 450 and 5% by weight of NG AR and NG 450 in KBr were prepared by grinding in a mortar and pestle to get a homogenous mixture. The absorption spectrum of each sample in plotted in Figure 3.5a. Figure 3.5b is the so-called Tauc Plot obtained from Figure 3.5a. The band gap value has been calculated using Tauc’s Equation (3) for an indirect band gap material7:

(3)

Where is the energy-dependent absorption coefficient, h is Planck’s constant, n is the photon’s frequency, *Eg* is the band gap energy, and B is a constant often termed as the band tailing parameter whose value changes with the material. The g factor depends on the nature of the electron transition; for an indirect transition, the value of g is equal to 2.A comparison of the band gaps of USR AR, USR 450, NG AR, and NG 450 which were reported in this study to be 3.33, 3.34, 3.26, and 3.26 eV, respectively, indicate no significant difference in band gap between calcined and as received catalyst. The absorbance of the USR catalyst appears higher after calcining. The approximately estimated band gap values are reported in Table 2. Both the USR and NG catalysts have band gaps that are comparable to reported literature values for anatase catalysts.23

Table 2. Band Gaps of Titania Catalysts

|  |  |  |  |
| --- | --- | --- | --- |
| USR AR | USR 450 | NG AR | NG 450 |
| 3.34 eV | 3.33 eV | 3.26 eV | 3.26 eV |

# Discussion

The literature presents conflicting views on whether sulfur enhances the photocatalytic activity of titania. These discrepancies in experimental results can be explained by the partially occupied sulfur-induced states which contribute to both hole-mediated (direct) and electron-mediated (indirect) pathways. Electron-hole pair formation can occur in two ways. The first is from UV light in which an electron is excited from the valence band to the conduction band leaving behind a hole in the valence band. The second occurs from visible light in which electrons are excited from partially sulfur-derived states into the conduction band, creating a hole in the sulfur states previously discussed by Rahmani *et al.*17 A previous study performed by Bakar and Riberio proposed that the doping of sulfur on titania enhanced the photodegradation of methyl orange through a hole-mediated pathway. It has been theorized that the enhanced photocatalytic activity from doping of sulfur in titania is due to the narrowing of the band gap,24 however, our study does not support this claim. Our study observed enhanced photocatalytic activity for both USR and NG upon calcination while the measured band gap was unchanged as reported in Table 1. Photonic yields for USR AR, USR 450, NG AR, and NG 450 were measured to be 39.9, 114, 36.0, and 93.0% respectively. The USR and NG material show an enhancement of rate after calcination by a factor of 2.86 and 2.58 respectively. These observations support the claim that the enhanced photocatalytic activity of sulfur-doped titania is not due to the narrowing of the band gap, but rather the introduction of deep sulfur-induced electron traps in the material. Calculations performed by Harb *et al.* found that at a concentration of 2%, the formation of the sulfur dimer is thermodynamically favored, which is fully occupied and does not influence the rate.25 Therefore, at low sulfur content, dimers are less likely to form, and the fraction of sulfur substituted on Ti lattice sites increases. By calcining the as-received titania catalyst, isolated sulfur atoms acting as deep electron traps are synthesized enhancing the photocatalytic activity between calcined and uncalcined material.

The optimal rate should be able to be accurately and reproducibly measured regardless of the photoreactor. This is because the optimal rate is a function of the light intensity corroborating the importance of adequately reporting the photon flux in photocatalysis studies. Measurements made for the USR and NG catalysts used a power supply that did not supply a constant current. As a result, kinetics measurements made in which the LED lamp was operated for 20 min > would fluctuate by ~100 mA unless monitored and corrected. Since the optimal rate is a function of light intensity and the light intensity is dependent on the current, these fluctuations can cause inaccuracies in the measured optimal rate. The discontinuity observed in Figure 11 for NG 450 could be due to these current fluctuations but may also be due to difficulty in separating the catalyst from the methyl orange solution using the centrifuge. The NG is denser than the USR and must be centrifuged several times to obtain a background that returns to the stock spectra’s baseline. To mitigate these sources of random error, the NG material must be remeasured using the designed constant current power supply and a higher rpm centrifuge that can better separate the material to obtain a more accurate mass dependence and optimal rate. As discussed previously, the photon flux measured by the integrating sphere is not physically reasonable with the relative power measurements made with the optical power meter. The power measured by the optical power meter with the filter is higher than the total power measured by the integrating sphere. This is because the integrating sphere is not collecting all of photons emitted from the LED nor all the wavelengths contributing to the reaction in the narrow distribution of the LED’s wavelength. It would be reasonable to believe that the integrating sphere is only measuring 10% of the contributing the photons leading to higher photonic yields than reported in the literature.22 The current photonic yield measurements prove that the integrating sphere can be used to make preliminary photon flux measurements utilizing a relative power calibration curve and a constant current power supply delivering 10 mA of current. The actual photonic yields are expected to be closer to 3.99, 11.4, 3.6, and 9.3% for USR AR, USR 450, NG AR, and NG 450 respectively. The photon flux measurements can be improved by using different wiring using a flat copper sheet so the entirety of the UV-LED can be inserted into the integrating sphere. Additionally, the integrating sphere software can be set to detect wavelengths of energy above the band gap of the titania catalysts.

Several engineering constraints must be considered in this project, the most pertinent being the safety and manufacturability of the UV-LEDs. The UV-LEDs have a current rating of 700 mA and will burn up if supplied with currents above this threshold. When designing the LM317 and S-LM317 circuits, it is necessary to test and design the circuits in a manner that this threshold will not be exceeded when using the UV-LED. To prevent high currents from being produced, variable resistors that are only able to produce a maximum current of 500 mA in the LM317 circuits were selected. This prevents the risk the erroneous adjustment of the variable resistor will result in damage to the UV-LEDs. Additionally, the UV-LED is not the device at risk of being burnt out due to high currents. The integrating sphere has a sensitive detector that will burn out at high light intensities supplied by the UV-LED. As a result, it was necessary to design a constant current power supply capable of providing a steady-state forward current of 10 mA to the UV-LED so that photon flux measurements could be made. The UV-LEDs also supply a wavelength of light that is harmful and can lead to damage to the eyes and cancer in humans if excessively exposed. Due to this safety constraint, photoreactors are designed with a safety box that blocks the operator from being irradiated with UV light. For photon flux measurements, the UV-LED facing the user is blocked with a black light-blocking fabric. When applying the UV-LEDs from the batch reactor system to the continuous stirred-tank reactor (CSTR) system several engineering constraints need to be considered. First, the CSTR is much larger than the batch reactor and requires a UV-LED lamp stick that is much longer. Second, the CSTR reactions are operated at the upper limit of the temperature rating for the UV-LED. This requires a high-power dissipating heat sink to be designed when applying the UV-LEDs to the CSTR.

# Conclusion

In this study, the photonic yield of two received and calcined sulfur-doped titania was preliminarily measured and used to quantify their photocatalytic efficiency in the context of the degradation of methyl orange. The measured photonic yields are 39.9, 114, 36.0, and 93.0% for USR AR, USR 450, NG AR, and NG 450 photocatalysts respectively. Overestimation of the photonic yield is most likely due to inaccuracies in the experimental procedure and are of measured values 10 times higher than expected. In addition, the data measured suggests that calcination of the titania photocatalysts to 450°C does not affect the band gap of the material with reported band gaps of USR AR and USR 450 to be 3.34 and 3.33 eV and 3.26 eV for both NG AR and NG 450. Photonic yields were used to determine an enhancement in photocatalytic activity of 2.86 and 2.58 between as received and calcined USR and NG respectively. This supports the idea that the enhanced activity observed for the calcined material is not due to the narrowing of the gap, but rather the synthesis of deep sulfur-induced electron traps in the structure of the material which aid in the electron-hole pair separation. Although the results suggest that sulfur doping in titania enhances the photocatalytic activity, a deeper understanding of the electron-hole dynamics is necessary. Research efforts as part of this project suggest the photon flux and optimal rate measurement techniques require further refinement to provide accurate and reproducible results. With the development of these improvements, these methods can be applied to more complicated systems such as the continuous stirred tank reactor for the photocatalytic conversion of methane to methanol. The future impact of this research can lead to solutions of environmental problems related to greenhouse gas pollution.

# References

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