**Elucidation of Photocatalytic Dynamics by Analysis of Transient Absorption Spectra**

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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 polices 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 the 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 population 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 percent of conversion.2,3

In the context of greenhouse gas conversion, the field of photocatalysis has become one of the most important disciplines of chemistry. Our study aims to continue work performed by previous research groups in photocatalysis by quantifying UV-LED driven photolysis of hydrogen peroxide. In the first phase of this project, we intend to improve methods for measuring and quantifying the photon flux of our single element UV LED. This will be done utilizing an integrating sphere for the measurements. We will solder a flat conducting material to the UV-LED to allow for the entire LED to be inserted into the integrating sphere, ensuring that every photon is measured by the detector. Additionally, we will remeasure the mass dependence of nanograpahi (NG) titania using a constant current power supply designed previously and a centrifuge that operates at a faster rpm than the one currently available to us. These improved methods in our mass dependence measurements should improve the data collected and illustrate a clear improvement in activity of our calcined and as received material.

Previous measurements of LED intensity as a function of If as measured by a silicon diode indicate a linear relation between photon flux and forward current (Figure 1A). The power supply designed in Phase 1 can be calibrated using this relation and applied in Phase 2 for design of a UV-LED lamp compatible with our preexisting continuous stirred-tank reactor (CSTR) depicted in Figure 1B.

A diagram of a diagram with blue dots

Description automatically generated

Figure 1. A) Integrated area of UV-Vis Peak vs. Forward Current; B) Proposed Photoreactor and LED Lamp

The UV-LED lamp provides several advantages over our Mercury-Vapor lamp; 1) the CSTR can be ran at a smaller volume and reducing the amount of 30% hydrogen peroxide being pumped to maintain steady state; 2) the smaller volume prevents methane gas from bubbling and entraining water into the lines of our GC-MS; 3) the UV-LEDs dissipate little heat in comparison to the Mercury-Vapor lamp making the need for cooling water lines obsolete. Using the photon flux calibrated UV-LED lamp and CSTR, the measurement of kinetics from the photolysis of hydrogen peroxide will be studied under two conditions in Phase 3. The first condition will study an aqueous hydrogen peroxide solution that optically has a small absorption, but no scattering effects. The second condition will study the same solution but with a titania catalyst present with both absorption and scattering effects.

We intend to study and gain a deep understanding of the electron-hole dynamics of our photocatalysts and correlate these dynamics with the experimental transient absorption spectra measured for these photocatalysts. We will investigate the literature for evidence of the mechanistic pathway of methyl orange occurring through a hole or electron mediated pathway. Once the mechanistic pathway is determined, we will develop a theory for the mechanism of the photocatalytic degradation determined from this literature search and transient absorption spectra.

References:

1 I. Karakurt, G. Aydin, and K. Aydiner, “Sources and mitigation of methane emissions by sectors: A critical review,” Renewable Energy **39**(1), 40–48 (2012).

2 Y. Tian, L. Piao, and X. Chen, “Research progress on the photocatalytic activation of methane to methanol,” Green Chem. **23**(10), 3526–3541 (2021).

3 L. Yuliati, and H. Yoshida, “Photocatalytic conversion of methane,” Chem. Soc. Rev. **37**(8), 1592 (2008).