Iron Modified Bismuth Titanate Pyrochlore Photocatalysts for Environmental Remediation and Solar Fuel Production

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

by

William C. Ragsdale

Dr. Vaidyanathan (Ravi) Subramanian/Thesis Advisor

May, 2016
THE GRADUATE SCHOOL

We recommend that the thesis prepared under our supervision by

WILLIAM C. RAGSDALE

Entitled

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MASTER OF SCIENCE

Dr. Vaidyanathan Subramanian, Advisor

Dr. Hongfei Lin, Committee Member

Dr. Dhanesh Chandra, Graduate School Representative

David W. Zeh, Ph.D., Dean, Graduate School

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Abstract

Photocatalysis represents an emerging field in material and chemical engineering that can provide solutions for specific problems in environmental engineering and sustainable energy production. What is unique about photocatalysis is that it represents a scope that combines traditional catalytic chemical engineering with electrochemical principles and techniques. Traditional catalysis involves the flow, transport, and adherence of reactants, typically in gas or liquid phase, to recyclable catalysts, while electrochemistry involves the extrusion of electrical charge carriers for direct electrical energy or redox reactions. Combining these two features allows us for a direct mechanism for converting sunlight into useable energy and lies directly under the purview of modern chemical engineers. Of particular interest in the field of photocatalysis are multi metal oxides due to their low cost of acquisition and band gap tunability. The work that follows represents three years of my time working in the SOLAR lab under the supervision of Dr. Ravi Subramanian developing novel mixed metal oxide photocatalysts to help alleviate environmental and energy related concerns.

In the first chapter we examine the catalytic activity of a pyrochlore phase bismuth titanate (Bi2Ti2O7-BTO) in driving the photo-assisted decomposition of a model pollutant, methyl orange (MO). The photoactivity of the BTO was probed with the inclusion of Fe with BTO and with the addition of a co-catalyst- Pt
external to the Fe-BTO. The addition of Fe was shown to enhance BTO photoactivity by ~38%, while the presences of Pt along with Fe demonstrated the most favorable increase at 74 % compared to the plain BTO. The MO degradation was analyzed following a pseudo first order kinetic rate law. Under 100% visible light illumination we note that all catalysts demonstrate photoactivity. Specifically, a 10%, 15%, and 21% degradation of MO with BTO, Fe-BTO, and Pt/Fe-BTO respectively, was observed. Stability analysis of the photocatalysts indicates that a mild oxidative treatment at 350°C is sufficient to recover ~ 80% of the photoactivity lost over 6 hours of exposure to photo-illumination in 2 h increments. Further, for the first time, complementary photo-electrochemical and optical measurement tools have been used to systematically probe the functioning of BTO in the presence of Fe and Pt. Electrochemical impedance, chronopotentiometry (intermittent illumination studies), and fluorescence measurements reveals Fe aids in visible light assisted charge separation, Pt is not as effective with visible light as it is with UV, and that a high concentration of hydroxyl radical in the Pt/Fe-BTO is the basis for improved photoactivity of the catalysts. Using bismuth titanate pyrochlore as a case study in this work, we demonstrate the approach to leverage optical and photoelectrochemical tools for systematic analysis of other multimetal oxides for future work.

In the second chapter we again examine the same catalyst, a pyrochlore based bismuth titanate (BTO) photocatalyst with incorporated Fe (Fe_BTO), for
the photocatalytic production of hydrogen. Detailed insights into the photocatalyst performance in a methanol-water mixture were obtained by examining the effects of catalyst loading, light intensity, methanol concentration, and catalyst stability under repeated use. Among the parameters examined, the hydrogen yield of 37 mL g\(^{-1}\) using 150 mg catalyst, 30,000 lux, and using methanol concentration of 20 M was determined the most effective for maximizing hydrogen generation. Additionally, all the time resolved hydrogen generation experiments indicated the presence of a methanol concentration dependent 2-zone region: zone 1 - slow hydrogen generation and zone 2 - rapid hydrogen generation. The existence of the 2-zone region is attributed to the role of the intermediates formed during the methanol oxidation process. The accelerated hydrogen generation is attributed to the formation of the intermediate formic acid, which is thermodynamically favored for rapid oxidation over methanol. Repeated use of the photocatalyst leads to over 70% loss in the Fe-BTO photoactivity. The productivity loss is attributed to the formation of surface-functional groups. The groups may be removed by a simple oxidative surface treatment to recover the photocatalyst without impacting the surface or physical properties of Fe-BTO.
Citations to Previously Published Work

A Portion of this thesis has appeared previously in the following paper:

“Photocatalytic activity of Fe-modified bismuth titanate pyrochlores: Insights into its stability, photoelectrochemical, and optical responses”,
William Ragsdale, Satyajit Gupta, Keenan Conard, Steven Delacruz, and Vaidyanathan (Ravi) Subramanian, Applied Catalysis B: Environmental, Volume 180, January 2016, 442-450
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Chapter 1

Photocatalytic activity of Fe-modified Bismuth Titanate Pyrochlores: Insights into its Stability, Photoelectrochemical, and Optical Responses

Introduction

Solar-driven environmental remediation of pollutants has traditionally been performed with oxide photocatalysts that consist of a single metal ion compounds as a base material – such as Ti in TiO$_2$.[1-3] To improve the oxides’ ability to facilitate enhanced photocatalytic remediation of environmental pollutants, a combination of oxide with other metal ions, zero-valent metal ad-atoms, metal oxides, or other photoactive entities, has been extensively studied.[4, 5] These combinations can allow for enhanced i) light absorbance,[6] ii) charge separation,[7, 8] and/or iii) broad band absorbance,[9] leading to improved
photoactivity. Unlike single metal oxides, the multi-metal oxides such as delafossite, sillenite, perovskite, or pyrochlores consist of structures that offer a unique benefit — the option to include additional elements (not including doping).[10, 11] The primary benefit with this option is the realization of an additional degree of freedom to include one or more additional element(s) that can aid with tuning the optical, electronic, and/or the photocatalytic properties.[12] The choice of elements in the structure can alter the band gap, direct/indirect properties, and the light mediated surface redox reactions.

Several mixed oxides have been tested in photocatalysis with their noteworthy applications in the areas of solar fuel generation and environmental remediation.[13-16] As a case study, we have examined the synthesis of a pyrochlore photocatalyst comprising of Bi and Ti as the primary elements.[17] Choosing Ti as the element for the B site, allows for the 3d orbitals to define the conduction band. On the same note, Bi as the element in the A site allows for establishing the valence band along with the O 2p orbital. This combination is unique because the overall band gap is determined to be 2.6 eV (Scheme 1-1) and it offers the possibility to perform wide ranging photocatalytic reactions and if needed, with visible light excitation as well. In previous work, we have evaluated the application of the BTO pyrochlore as a hydrogen evolution photocatalyst with water-methanol mixtures.[18, 19]
In a related study Yao et al., have shown that rare earth element such as La can promote the photodegradation of textile dye using bismuth titanate.\cite{20} A rigorous density functional theory study, or DFT analysis, on pyrochlore BTO and a series of elements belonging to the 3d group has determined that inter-band states can be created in the BTO that will affect optical absorbance.\cite{12} Since these multi-metal oxides offer a band gap tunability option, we refer to these compounds as band gap engineered composite oxide nanostructures or BECONs. We have validated the modeling predictions by showing that pyrochlore BECONs containing earth abundant 3d elements such as Fe, Mn, Co, or Ni can promote the photoactivity of BTO and also showed preliminary experimental results.
demonstrating the benefits of such 3d element addition to BTO.[12, 21] Though these preliminary modeling results are promising, several aspects of BTO based multi-element BECONs still remain to be fully understood. Before exploring the applicability of other elements as building blocks by following a rather Edisonian pathway, one needs to understand i) if these photocatalysts comprising of earth abundant elements how does the inclusion of a 3rd element influence the environmental remediation aspect of the BTO, ii) how does the addition of external ad-atoms to this mix, a highly beneficial step for single metal oxides, influence photoactivity, and iii) if it is possible to explain the activity of these catalysts using photoelectrochemical techniques.

In this work, we report on the application of BTO composite with Fe as a case study for the remediation of an environmental pollutant Methyl Orange, to answer the aforementioned questions. Firstly, the optimization of the Fe-BTO photoactivity has been performed by examining catalyst loading and dye concentration effects. Secondly, the improvement in the photoactivity of this Fe-BTO BECON due to the addition of a co-catalyst, Pt, a well-known promoter of photoactivity, has been examined, under the optimized experimental conditions. Thirdly, the photoactivity of the BECONs upon sustained use has been examined by performing repeat experiments to correlate surface properties with photoactivity. To determine application potential, the activity of all photocatalysts has also been examined under 100% visible light illumination. Finally, we have performed optical and
photoelectrochemical studies to understand and correlate the interfacial relative oxidative properties of all the photocatalysts.

I. Experimental Section

Materials:

The synthesis was carried out using precursor chemicals obtained from local suppliers. Nitric acid ACS, BDH3046-2.5LPC, 68%, BDH Aristar), bismuth nitrate pentahydrate (ACS, 98%, Alfa Aesar), titanium (IV) isopropoxide (97%, Sigma-Aldrich), Iron(III) nitrate nonahydrate (ACS, >98%, Sigma-Aldrich), and ammonia solution (A667-212, >25%, Fisher Scientific) were all purchased from the commercial vendors respectively. Stock solutions of 1M Nitric Acid, 0.1M bismuth nitrate, 0.1M titanium isopropoxide, and 0.1M iron nitrate were prepared. Deionized water from Millipore® system was used to dilute and wash all precipitates formed.

Photocatalyst synthesis:

0.1 M solution of each of the precursors were taken in an acidified medium (HNO₃ as solution) and mixed together in stoichiometric proportions as shown in the supplementary information, Figure 1-1. After thorough mixing for 10 minutes the pH of the solution was changed by the addition of ammonium hydroxide leading to the formation of a yellowish-white solid precipitate. The solid was
ground into a fine powder and mildly heat treated to remove organics. High temperature thermal treatment was then performed at 600°C for 6 h to facilitate phase transformation. In the experiments involving Pt, Pt was deposited by photo-reduction of an aqueous Pt salt solution by irradiation in the presence of the BTO.

**Figure 1-1:** The sequence of steps used for the synthesis of the BTO and Fe-BTO (1% Fe) composite photocatalysts.

**Surface analysis:**

Phase analysis of the photo-catalysts was carried out using an XRD instrument [Philips (model: 12045 B/3X-ray diffractometer) with Cu K-alpha as X-ray source]. The surface analysis was performed using microscopy, optical spectroscopy, and photoelectrochemistry measurement tools. SEM (Hitachi® S-4700) was used to examine the physical features of the oxide nanoparticles. TEM (JEOL® 2100F) was used to determine the particle size. Optical
absorbance measurements were carried out using a UV–visible spectrophotometer (Shimadzu UV-2501PC) to determine the photocatalysts stability before and after usage. Films of the photocatalyst were prepared on conducting glass slides for photoelectrochemical (PEC) measurements. These measurements were performed on the photocatalyst film using an Autolab Potentitonstat/Galvanostat to gather chronoamperometry and chronopotentiometry data.[22] A Xenon lamp was used as the light source in an optical train consisting of a setup detailed elsewhere.[23]

**Photocatalysis experiments using slurry reactor set-up:**

The photoactivity of the Fe-BTO, with and without Pt, was examined using a slurry reactor of 500 mL volume with a jacketed cooling option. The reactor details are described elsewhere. [24] A 250 mL of an aqueous solution of methyl orange with concentrations of 10 and 20 μM was used as the model pollutant. A Xe lamp with a 300 W output power was used as the light source in all experiments. In the case of the visible light mediated photocatalytic dye-degradation experiment, a FRS-GG400 filter from Newport® and 0.5 M CuSO₄ solution was used in the light source to cutoff the UV region. The changes to the irradiated solution were noted using spectroscopy at regular intervals of time. All solutions were irradiated in an oxygen environment. The photocatalysts were decanted, dried, and reused to determine their reproducibility. All photocatalytic experiments were performed in duplicate to ensure reproducible trends.
II. Experimental Results

**Structural and compositional characterization of the photocatalyst:**

*Figure 1-2A* shows the XRD of the synthesized photocatalyst. The XRD peaks are indexed using the JCPDS Card # 32-0118. The peak at 28.7° corresponds to the 622 plane and 29.9° corresponds to the 444 plane of BTO. *Figure 1-2B* shows the absorbance spectra of Fe-free BTO and 1% Fe_BTO. A significant red-shift is observed, indicating that the presence of iron within the BTO enhances the visible light absorption through a shifting of the onset absorbance by approximately 100 nm. This shift into the visible region is a critically desirable component when developing and designing visible light activated photocatalysts. The band gap was calculated from the UV-Vis spectra using the relationship $E = \frac{hc}{\lambda}$, applied at the onset. The shift in the onset of absorbance has the effect of lowering the band gap by 0.4 electron volts from approximately 2.8 eV to 2.4 eV. This trend of decreasing the band gap with a third element addition is in agreement with earlier results obtained using pseudo-plane wave density function modeling studies on these types of multimetal oxide photocatalysts.[12, 25] Of noteworthy importance from the XRD analysis is that the catalysts prepared with 1% Fe do not show any Fe-based oxide suggesting that the Fe is a part of the BTO. *Figure 1-3A* and *Figure 1-3B* shows the SEM and TEM images respectively of the 1% Fe_BTO. The SEM indicates that the
physical shapes of the particles are similar and they are well dispersed (not aggregated). The TEM provides a clearer image of the catalyst size indicating an average diameter of 10±4 nm.

Figure 1-2: The characterization of the photocatalysts using (A) XRD indicating the crystalline nature of the thermally treated (a) BTO and (b) Fe_BTO (1 wt %) and (B) absorbance spectroscopy showing the response of (a) BTO and (b) Fe_BTO indicating a red-shift with Fe addition.

Figure 1-3: The (A) SEM image of a representative sample area of Fe_BTO (1 wt %) indicating the particle features, (B) TEM image indicating the photocatalyst size of 10±4 nm.
Effects of the catalyst loading on MO conversion with Fe-modified BTO:

The effect of catalyst loading on the photoconversion of the MO was examined at a dye concentration of 10 µM. Negligibly small aliquots of the dye were removed from the slurry reactor and the absorbance was checked at regular time intervals. A consistent decrease in the peak absorbance of the dye at ~ 450 nm was noted over time (Figure 1-4), without any additional peak formation. Control experiments with the dye in the catalyst absence (Figure 1-5) indicates no degradation of MO, demonstrating that dye photolysis does not occur and the catalyst is instrumental in effecting the conversion of the dye. Figure 1-6A shows a plot of the conversion of the dye against time for different catalyst loadings. The conversion was calculated from the absorbance spectra and normalized to the initial concentration. An optimal loading of 150 mg is noted to be most effective for this system, facilitating a ~53% dye conversion over a 2 h period.

![Figure 1-4](image-url): The time resolved absorbance plots of methyl orange (MO) over a duration 120 min collected after illumination of 150 mg of the Fe_BTO (1 wt%) photocatalyst.
Effects of the dye concentration on the photoactivity of the Fe-modified BTO:

The effect of the dye concentration was examined at the optimal loading of 150 mg. Increasing the dye concentration from 10 μM to 20 μM demonstrated a decrease in the conversion of the dye over a 2 h period as shown in Figure 1-6B. This observation may be attributed to light screening effect of the dye, and/or reduced availability of active catalyst sites for MO molecules for adsorption and reaction.[26] Further, it has been noted that in both dye concentration experiments, the presence of Fe yields a higher conversion of the dye compared to Fe-free BTO. The increased activity with the Fe presence is attributed to the greater visible light
absorbance, which leads to more e-h pair generation, proving that Fe addition is beneficial.

Figure 1-6: Shows the degradation profile of MO solution with (A) various catalyst loadings of Fe_BTO (1 wt %) in the presence of a 10 µM dye solution and (B) BTO and Fe_BTO (1 wt %) and a MO concentration of 10 µM and 20 µM.

Boosting the performance of the photocatalyst with Pt addition:

It is well known that the addition of metals such as platinum or gold as a co-catalyst can improve the photocatalytic activity of single metal oxides as indicated with the extensive studies with TiO$_2$.[27, 28] The improvement in activity is attributed to the ability of the metal to aid in separation of charges which promotes hole availability for oxidative reactions.[6, 7, 29] Pt was added to the Fe-BTO to examine the co-catalyst effect on MO oxidation. The time resolved photographs indicate an almost complete loss of color of the dye after illumination (Figure 1-7A). At a Pt loading of ~1 wt %, the photoactivity of the Fe-BTO was noted to
increase by 74% within the 2 h illumination period as shown in Figure 1-7B. Such a boosting effect confirms that the co-catalyst activity, noted with single metal oxides, is also observed with multimetal oxides, and that the Pt functions as an electron sink leading to the freeing up of more holes that promote the oxidation of MO.

**Figure 1-7:** (A) The photographs shows the time resolved absorbance spectra of the dye solution over a 2 h duration and (B) shows the degradation profile of a 10 µM MO dye solution in the presence of Fe_BTO (1 wt%) and Pt/Fe_BTO (1 wt%).
**Kinetic analysis of the photoactivity of Fe-BTO and Pt/Fe-BTO:**

The kinetics of the MO conversion was analyzed using a pseudo steady state first order lumped parameter model.[11, 23] The rate constant of the reaction were determined by linearization of the conversion data shown in Figure 1-6 and 1-7B. **Table 1-1** summarizes the corresponding rate constants (Figure 8 shows the results of linearization) for each of the experiments. The values are of the order of $10^{-3}$ min$^{-1}$, with the maximum rate constant observed for the degradation of MO using Fe-BTO in the presence of the Pt deposits. The trends in the results are consistent with those noted in earlier reports.[23, 26] From a mechanistic standpoint, the fact that the dye absorbance decreases monotonically, suggests that the MO degradation process on Fe-BTO and Pt/Fe-BTO follows an established mechanism discussed elsewhere.[30, 31]

<table>
<thead>
<tr>
<th>Catalyst with various dye concentration and amount used</th>
<th>Pseudo first order rate constant, k (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO 10 μM, 150 mg BTO</td>
<td>0.00251</td>
</tr>
<tr>
<td>MO 20 μM, 150 mg BTO</td>
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<tr>
<td>MO 10 μM, 100 mg Fe_BTO (1 wt%)</td>
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<tr>
<td>MO 10 μM, 200 mg Fe_BTO (1 wt%)</td>
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<td>MO 20 μM, 100 mg Fe_BTO (1 wt%)</td>
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</tr>
<tr>
<td>MO 10 μM, 150 mg Pt / Fe_BTO (1 wt%)</td>
<td>0.01568</td>
</tr>
</tbody>
</table>

**Table 1-1:** The values of the rate constants for the MO degradation using a pseudo first order lumped parameter kinetic model is shown. The rate constants were estimated from the conversion data of Figures 3 and 4.
Figure 1-8: The pseudo first order kinetics analysis of (A) 10 μM methyl orange (MO) with Fe_BTO (1wt %) and BTO (B) 20 μM MO with Fe_BTO (1wt %) and BTO (C) 10 μM MO with various Fe_BTO (1wt %) loading, and (D) 10 μM MO with Pt/Fe_BTO (1wt%) and Fe_BTO (1wt%).

Stability of the photocatalysts:

The photocatalysts’ were recovered after the first 2h run by centrifugation and then subjected to drying. They were used with a fresh solution of the dye and tested for another 2h for their activity. Figure 1-9A shows the fractional conversion
of the dye after 3 such repeated runs over a 6h period. The second and the third runs show a progressive decrease in the fractional conversion of the dye. Absorbance spectra of the used photocatalyst are shown in Figure 1-9B. Images of the photocatalysts before and after MO conversion show a change in the coloration (Figure 1-9C). For recovery studies, the catalyst was subjected to a mild thermal oxidative treatment at 350°C. When this treated photocatalyst was used again for MO conversion (Figure 1-9A, “recovered”), the recovery in the activity becomes evident. The absorbance spectra of the treated photocatalyst (Figure 1-9B) also show a profile similar to the unused photocatalyst. This recovery of the photoactive sites can be attributed to the oxidative removal of intermediates produced and deposited during the photocatalysis. In related literature besides oxidative treatment, alternate approaches such as photo-irradiation, thermal treatment, or chemical treatment have also been reported for activity recovery.[32, 33]
**Figure 1-9:** (A) The time resolved decrease in the MO concentration ($C_t/C_0$) in the presence of the photocatalyst after each use over 3 cycles and a 4th “recovery” cycle, (B) The absorbance spectra of (a) pristine Fe_BTO (1 wt%), (b) Fe_BTO (1 wt%) after 3rd run and (c) after heat treatment, showing the recovery of the surface after heat treatment (C) Photograph of the photocatalyst, (a) before and (b) after heat treatment.

**Visible light activity:**

The visible light activity of the catalysts was examined using UV cut-off filters (discussed in the experimental section) in the path of the light source. A 2 h continuous illumination indicates a fractional conversion of 10%, 15%, and 21% of the dye in the presence of BTO, Fe-BTO and Pt/Fe-BTO respectively. This activity can only be possible due to the visible light photons absorbed by the presence of Fe (as discussed earlier, Fe-BTO showed a 100 nm red-shift in the absorbance, compared to BTO). Of noteworthy importance is the result that the presence of Pt
offers only a marginal improvement of 6% and Pt is not as effective as it is under UV-Vis illumination (~20%). In a related work, the visible light-driven MO photodegradation has been demonstrated with Bi-Fe-Nb composites.[34] The choice of Nb establishes a higher level conduction band compared to Ti. Thus, our work and this literature, suggest that 100% visible light driven activity is possible with Fe inclusion, and is a step in the right direction towards visible light active photocatalyst design. However, further studies need to be undertaken by considering the inclusion of other elements within the BTO.

III. Discussion

**Photoelectrochemical insights:**

Photoelectrochemical or PEC measurements provide insights into the effects of the application of external driving forces, such as potential, on the transport of charges within photocatalyst films.[35] The PEC measurements of the photocatalysts, immobilized on ITO-coated conducting glass slides, were performed using a 0.1 M sodium hydroxide (NaOH) solution as electrolyte. The chronopotentiometry (V/t) responses of the films under periodic on-off illumination were performed to determine the rapidity of charge separation in the photocatalyst. **Figure 1-10A** indicates the instantaneous response to illumination. A step function response shows that electron – hole pairs are instantaneously generated and remain separated. A control experiment with a TiO₂ film was also performed. It indicates the typical n-type characteristic with the increasing
voltage. Further, MS analysis was performed using the BTO film. Contrasting the result from the BTO experiment with the TiO$_2$ control and the MS analysis, it can be concluded that the BTO demonstrates an n-type characteristic. Since Fe-BTO comprises of earth abundant elements and can be prone to corrosion, extended illumination effects was also examined. Continuous illumination of the film shows almost constant voltage of $\sim$46 mV indicating that the response is because of the photogenerated electrons. This result along with the absorbance of the photocatalyst shows that the BTO synthesized by the method presented here is not prone to structural destabilization by corrosion.

The V/t response of the Fe modified BTO presented in Figure 1-10B shows two interesting responses. Firstly, the direction of the flow of current is opposite to the direction noted with Fe-BTO. This indicates that the presence of Fe makes the Fe-BTO display a p-type characteristic. Secondly, though the response to continuous on-off cycles is instantaneous, unlike BTO films the magnitude of the voltage is not constant and gradually increases. However, continuous illumination suggests that the voltage passes through a maximum and then stabilizes as shown in Figure 1-10B. Finally, the decay of the voltage is also relatively much slower compared to the BTO. These observations indicate that Fe is playing a role in the movement and trapping/detrapping of the photogenerated electrons. The results with Pt deposits on the Fe-BTO are shown in Figure 1-10C. The responses are identical to the results seen with Fe-BTO in Figure 1-10B. Interestingly the voltage does not pass through maxima as evident with Fe-BTO. The $\Delta V$ associated with
each of the films containing the Fe or Pt is ~15% higher than the one noted with BTO as indicated in Table 1-2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta V$, (V)</th>
<th>Fluorescence Intensity (A.U.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTO</td>
<td>0.043</td>
<td>18,974,040</td>
</tr>
<tr>
<td>Fe_BTO (1 wt%)</td>
<td>0.046</td>
<td>19,776,800</td>
</tr>
<tr>
<td>Pt/Fe_BTO (1 wt%)</td>
<td>0.048</td>
<td>33,245,460</td>
</tr>
</tbody>
</table>

Table 1-2: $\Delta V$ [measured from chronopotentiometric (V/t) analysis] and fluorescence signal intensity [of 2-hydroxyterephthalic acid (TAOH), measured at 426 nm] for various photocatalysts, BTO, Fe_BTO (1wt% Fe) and Fe_BTO with Pt.

Figure 1-10: Chronopotentionmetric (V/t) traces of (A) BTO, (B) Fe_BTO (1 wt%), and (C) Fe_BTO (1 wt %)/Pt. The measurements were performed using a three electrode setup with 0.1 M NaOH as an electrolyte.
**Electrochemical impedance analysis:**

Electrochemical impedance spectroscopy (EIS) measurements offer insights into the effectiveness of the photocatalyst to separate the photogenerated charges.[36, 37] The EIS measurement was performed using the photocatalyst films prepared on conducting glass (ITO) in the presence of aqueous Na$_2$SO$_4$. A plot of the imaginary and real coordinates for the films in the presence and absence of photoillumination is shown in **Figure 1-11**. The greater the radius of the arc, the lower the extent of interfacial charge transfer occurring within the system.[36] A comparison of Fe-BTO with the BTO indicates that the charge separation is greater with Fe_BTO than BTO, attributable to the Fe presence. The increased activity of the BTO observed in the results section can be correlated to the improved charge separation resulting in greater availability of holes for oxidation. A similar observation was noted in earlier studies on single metal oxide photocatalysts involving Fe doped TiO$_2$[38] and Fe doped graphitic C$_3$N$_4$.[39]
Figure 1-11: The plot of the $Z_{\text{imag}}$ vs. $Z_{\text{real}}$ obtained using EIS measurements of the films are shown in the figure. The films made of BTO and Fe_BTO on conducting glass evaluated using 0.2 N Na$_2$SO$_4$ solution as the electrolyte in the absence and presence of illumination.

Probing of *OH concentration using fluorescence:

The hydroxyl radical (*OH) is a strong oxidizing intermediate that aids in environmental remediation.[40] Its formation, via $h^* + \text{OH} \rightarrow *\text{OH}$, is critical to the initiation of the oxidative mineralization of the MO.[41] Therefore, probing its concentration in the presence of various photocatalysts (BTO, Fe-BTO and Pt/Fe-BTO) will provide additional insights into how the presence of Fe and Pt influence *OH availability under illumination. The formation of the reactive *OH can be
tracked using terephthalic acid (TA) as a probe in fluorescence spectroscopy.[42, 43] In this experiment, the photogenerated \( \bullet \)OH react with terephthalic acid (TA) and forms a fluorescent 2-hydroxyterephthalic acid (TA-OH). In a typical experiment, the photocatalyst is mixed in a basic TA solution (in water) and then charged with the same light source used for the photodegradation experiment. The emission spectrum (measured at 424 nm) corresponding to TA-OH was measured after a time interval of 45 min. Table 1-2 shows the relative fluorescence signal intensities of the TA-OH generated during the course of the reaction with various catalysts. The intensity follows the order: Pt/Fe-BTO > Fe-BTO > BTO, indicating that the largest amount of hydroxyl radicals is generated in the presence of Pt/Fe-BTO. This observation confirms that the holes are produced and available at its optimal level in the presence of Fe and Pt and validates the trends in the photocatalysis studies.

**Insights into the mechanism of charge trapping /detrapping in the Fe-BTO and Pt/Fe-BTO photocatalyst:**

From the observations in the results and discussion sections, the photogenerated charge trapping/detrapping in Fe-BTO and Pt/Fe-BTO can be summarized as illustrated in the Scheme 1-2. The absence of Fe or Pt leaves the BTO as an ineffective photocatalyst due to severe charge recombination (1-2a). The presence of Fe in the Fe-BTO imparts a beneficial effect in the photocatalytic degradation of MO by (i) serving as a ‘localized’ electron-trap
center and (ii) promoting the photodegradation of MO compared to BTO (1-2b).

The former aspect of Fe presence was probed using light-induced photovoltage measurement as a function of time. The electron trapping phenomena in Fe-BTO is indicated from the decay characteristic of the photovoltage, after reaching a peak value under constant photo-illuminated condition. This critical response is reproduced in the multiple on-off cycles of the photovoltage vs time trace. The electron-trapping phenomenon prevents the electron-hole recombination and enhances the hole-life time for oxidative reactions to generate higher \( \cdot \text{OH} \) concentration, compared to BTO. The increase in the reactive \( \cdot \text{OH} \) concentration was indicated from the terephthalic acid or TA experiment.

Furthermore, Pt (noble metal) deposition at the Fe-BTO surface results in the buildup of the voltage, after photoillumination, as indicated in Figure 1-10C. This specific behavior is due to the electron accumulation at the surface ‘Pt’ centers, acting as ‘electron-sink’. This, effect is further beneficial for photo-remediation, as it boosts the hole-lifetime and significantly increases the reactive OH concentration (probed using TA experiment) compared to Fe-BTO, which is responsible for a greater MO degradation. A more roundabout mode for hydroxyl radical generation using the electrons trapped in Pt can occur via a superoxide anion (1-2c). However, this contribution is predominant only under UV-vis illumination (~30%) compared to visible illumination (~6%).
Scheme 2 shows the summary of the effects evident as a result of the inclusion of Fe and Pt identified from the photoelectrochemical, fluorescence, and photocatalysis measurements.

Finally, the Fe addition to BTO raises two further questions: (1) What if Fe is present as Fe$_2$O$_3$ at the BTO-oxide surface (note that the absence of Fe$_2$O$_3$ peaks in the XRD cannot conclusively rule out a very small Fe$_2$O$_3$ content) and if does, how will it impact performance? and, (2) What is the site in which the Fe is incorporated (Bi- or Ti-) and how does it affect performance? Even if there is Fe$_2$O$_3$ presence on the surface, Fe$_2$O$_3$ is limited in its ability to contribute to photoactivity by itself (very high recombination rates); it has to coexist with another catalyst with straddled band energetics.[44, 45] This aspect has to be probed using HRTEM.
the case of the latter, further studies (for example using EXAFS/XANES) are required to probe the structural form of Fe_BTO studied in this work. This structural understanding will aid in further understanding of the photoactivity of these composites.

**Conclusion**

This work presents a detailed analysis of the photocatalytic activity of a pyrochlore photocatalyst comprising of earth-abundant elements, Bi, Ti, Fe, and O in the form of bismuth titanate (BTO and Fe-BTO) as well as the effects of Pt addition as a co-catalyst. A series of inter-related studies involving the evaluation of the effects of catalyst loading, light intensity, dye concentration, and the decoupling of the visible and UV light effects - physicochemical factors that underline the performance of the photocatalyst - have been systematically investigated using a slurry-based reactor configuration. Photoelectrochemical analysis performed using impedance measurements (EIS) and photovoltage (V/t), for the first time, sheds light into the role of Fe as a center promoting the separation and trapping of photogenerated charges in the Fe-BTO and Pt/Fe-BTO systems. Further, from a photocatalyst stability standpoint, repeated use indicates a continued reduction in the photocatalyst performance in subsequent cycles. A simple post-use oxidative treatment is very effective in purging out these groups without imparting any detrimental transformation in the optical and/or physical features of the photocatalyst. This work sets the protocol for the systematic and
detailed testing of other forms of multi-metal oxides such as delafossites, sillenite, spinels, or perovskites in photo-driven chemical reactions.
Chapter 2

Insights into the Photocatalytic Activity of Iron Modified Bismuth Titanate in Photocatalytic Hydrogen Generation

Introduction

Hydrogen represents a clean and potentially unlimited energy resource for use in typical combustion reactions as well as in the successful hydrogen fuel-cells market. Techniques to produce clean, eco-friendly, and cheap hydrogen efficiently will be required as we attempt to bridge the gap between the age of hydrocarbons as our primary fuel source to a more renewable and sustainable energy fuel. There is the potential for an unlimited energy source using solar activated catalysts to produce hydrogen along with other products from water splitting or other sacrificial agents.[1-9] The hydrogen can then be separated and harvested for useful energy production with the benefit of being utilized in a zero-emission cost-effective system. The challenges in developing these catalysts include: (i) ensuring that the catalysts can indeed be activated empirically utilizing UV visible light, (ii) enhancing
charge (electron-hole) separation before recombination, and (iii) providing a long enough useful life of the catalyst for economic feasibility.

A large volume of research has been carried out on specifically tailored catalysts in order to achieve empirical water splitting in a photocatalytic reaction.[10-16] TiO$_2$ was one of the first photo-activated catalysts that was studied for its effects in areas concerning light harvesting and water splitting.[17-19] It is important to note that, the band gap of TiO$_2$ [$E_g=3.2$] is large, which restrict the applications of photo-activated redox reactions of TiO$_2$ to the UV range of the electromagnetic spectrum. Despite this, TiO$_2$ still remains as a benchmark to which all semiconductor catalysts can be measured against. Specific to photocatalytic H$_2$ generation, other oxide based materials such as, Fe$_2$O$_3$ [20], SrTiO$_3$[21], WO$_3$[22], Bi$_2$WO$_6$[23], Cu$_2$O[24], Ba$_5$Ta$_4$O$_{15}$[25], and non-oxides such as, C$_3$N$_4$[26], and silicon nanowires[27] have recently been studied.

The pyrochlore family of oxide compounds (A$_2$B$_2$O$_7$) represent some of the promising semiconductors ($E_g=2.8$ eV) in photocatalysis. It allows for the option to design the A$_2$O octahedral site within the pyrochlore, which facilitates the tailoring of the band gap to the requirements of any photodriven application (Scheme 2-1).[28,29] Should pyrochlore photocatalysts be synthesized with a band gap between 1.6-2.8 eV it can be a promising candidate not just for water splitting, but for other photo-assisted processes such as CO$_2$ reduction.[30] To pursue this concept one representative compound, bismuth titanate-BTO, was chosen since the electronic effect of the bismuth 6s$^2$ electrons can be leveraged to
narrow the band gap. Furthermore, pyrochlore structures also provide high temperature stability and are economically attractive since they can be comprised of cheap, earth abundant materials.[31]

We have pursued in the direction set forth in the above paragraph and reported on those efforts, recently. We have developed what we refer to as band gap engineered composite oxide nanostructures (BECON) using BTO that can (i) be produced with tight size control[32] and varying aspect ratio[33], (ii) be thermodynamically compatible and stable with a series of 3d transition elements as indicated from pseudo-plane wave density function calculations[29], (iii) be synthesized with the 3d elements using wet chemical techniques and, (iv) demonstrate UV-visible light absorbance in the sweet spot of 1.6-2.8 eV along with proof-of-concept application towards photo-assisted hydrogen generation using an aqueous solution of a sacrificial agent.[33] The Scheme 2-1 summarizes the properties of the BECONs and compares it with the benchmark TiO₂ photocatalyst.
Scheme 2-1: The energy band-edge positions of the band gap engineered composite oxide nanostructures – BECONs – relative to the global standard TiO₂ is shown. The redox potential of reactions of interest to solar – driven photocatalytic processes is also shown indicating the potential multifunctionality of the BECONs.

However, there are several questions that remain unanswered and are crucial for a complete understanding of the photoactivity of the pyrochlorel BECONs. These are: How does the products of photocatalysis using pyrochlore and sacrificial agent influence hydrogen evolution? To what extent is the sacrificial agent contribution important in the photoactivity of the pyrochlore? How stable are the pyrochlore photocatalyst? and what parameter, if any, affects its stability? The 3d element Fe included BTO pyrochlore is examined as a case study to answer these questions. This work draws from the insights obtained in a series of catalyst optimization experiments followed by optical and surface characterization analysis.
I. Experimental Section

**Materials:**

The synthesis was carried out using precursor chemicals obtained from local suppliers. Nitric acid ACS, BDH3046-2.5LPC, 68%, BDH Aristar), bismuth nitrate pentahydrate (ACS, 98%, Alfa Aesar), titanium (IV) isopropoxide (97%, Sigma-Aldrich), Iron(III) nitrate nonahydrate (ACS, 98%, Sigma-Aldrich), and ammonia solution (A667-212, ≥25%, Fisher Scientific) were all purchased from the commercial vendors respectively. Stock solutions of 1M Nitric Acid, 0.1M Bismuth Nitrate, 0.1M Titanium Isopropoxide, and 0.1M Iron Nitrate were prepared. Pure deionized water was used to dilute and wash all precipitates formed.

**Photocatalyst synthesis:**

The synthesis procedure is given in Figure 1-2. 50 mL of 0.1M titanium stock solution (titanium stock solution was prepared from titanium isopropoxide using nitric acid solution), 49.5 mL of 0.1M bismuth nitrate, and 0.5 mL of iron nitrate were added under acidic conditions and the solution was stirred. The pH of the solution was then slowly raised by the addition of concentrated ammonia until all oxide species precipitated out of the mixture. The resulting powder was washed with deionized water and centrifuged to remove all supernatant. The oxide precipitates were dried at 150°C for 6 hours. The dried solid was finely ground via mortar and pestle and was then annealed at 600°C for 6 hours (2 hour ramp time
with a 1 hour return time). As a control BTO was also synthesized by following the same procedure. The procedure was followed exactly as stated above, without the inclusion of iron nitrate. This produced an equimolar BTO pyrochlore that was used to provide a benchmark for the Fe_BTO to be compared against for hydrogen evolution in the reactor.

**Surface, morphological, and optical characterization:**

Phase analysis of the synthesized photo-catalysts was carried out using an XRD instrument [Philips (model: 12045 B/3X-ray diffractometer) with a scan rate of 0.03°/min and Cu K-alpha was used as X-ray source]. A Hitachi®S-4700 scanning electron microscope (SEM) was used to determine the surface features of the as synthesized Fe_BTO powder. The powder was coated over carbon tape prior to analysis. A JEOL® 2100F high resolution transmission electron microscope (HRTEM) was used to examine the morphological features of the samples. The optical absorption properties of the BTO and Fe_BTO were examined using a UV–visible spectrophotometer (Shimadzu UV-2501PC) with a wavelength variation from 300 to 800 nm. The absorption properties of the powders were studied in film form by coating them over glass slides. The powders were first dispersed in a solution containing an acetonitrile/water mixture. After that Triton X, was added and it was coated over the glass slides and heated to 400 °C to burn the organics off and obtain uniform films. These films were then used in the absorbance measurements. The EIS measurements of the catalysts were
performed using a Gamry electrochemical workstation using a three-electrode apparatus. The photocatalysts were coated over ITO glass slides, served as the working electrode, with a platinum wire as the counter electrode and Ag/AgCl (in 3.4 M KCl) as the reference electrode and was performed in the presence of a 0.2 M Na₂SO₄ solution.[34] This was carried out in dark and light illuminated condition. A 500 W Newport Xenon arc lamp was used as a light source with an intensity of ~100 mW/cm².

**Photocatalysis Experiments:**

The reactor used in the photocatalyst activity measurements consisted of a 450W Hg vapor lamp immersed inside a water-cooled annulus. The batch reaction occurs in the bottom 40% of the vessel around the annulus with a constant stirring rate in order to minimize spatial variations. The batch reactor was connected to a downward displacement column filled with water for collection of the product gas as well as providing an accurate determination of the volume of gas evolved during the experiment. An actuator with a moveable “T”- valve was connected to the top of the column to allow for sampling of the evolved gas. 1 mL samples of the reaction products were taken at 30 minute intervals for a total of 130 min and injected into an SRI 6345 Gas Chromatograph for quantitative analysis. The first sample was taken at 10 min in an effort to investigate initial reaction parameters.
II. Experimental Results

**Structural characterization of the photocatalyst:**

*Figure 2-1A* and *2-1B* shows the SEM and TEM images respectively of the 1% Fe_BTO. The SEM indicates that the particles are fairly uniform, with most of them showing a spherical morphology. The TEM provides a more clearer image of the catalyst size indicating an average diameter of 10±4 nm The lattice fringes can be observed from the HRTEM image (*Figure 2-1C*), which suggests a ordering with a high degree of crystallinity. The high resolution fast Fourier transformation (FFT) analysis (*Figure 2-1C Inset*) indicates a “$d$-spacing” value of 3.2 Å, corresponding to the 622 plane of the BTO. Further, to examine the iron content in the Fe-BTO samples, EDAX analysis was carried out with the catalysts (*Figure 2-1D*). The presence of Fe is evident from the analysis and its composition relative to the other elements detected (Bi, Ti, and O) is given in the table of *Figure 2-1D*. 
Figure 2-1. The (A) SEM image of a representative sample area of Fe-BTO (1%) indicating the particle features, (B) TEM image indicating the BTO nanoparticle size of 10-15 nm, and (C) high magnification image indicating the crystalline nature of the Fe-BTO (as evidenced from the SAED result of the inset). The Figure (D) shows the EDX results of the qualitative and quantitative analysis identifying the elements present in the photocatalyst.

Figure 2-2A shows the XRD of the synthesized photocatalyst. The XRD peaks are indexed using the JCPDS Card # 32-0118. The peak at 28.7° corresponds to the 622 plane and 29.9° corresponds to the 444 plane of BTO. The highest intensity peak at 2Θ = 29.99° confirms the HRTEM observations indicating bismuth titanate with the pyrochlore structure.[33] Figure 2-2B shows the absorbance spectra of Fe-free BTO and 1% Fe_BTO. A significant red-shift is
observed indicating that the presence of iron within the BTO enhances the visible light absorption through a shifting of the onset absorbance by approximately 100 nm. This shift into the visible region is a critically desirable component when developing and designing direct sunlight activated photocatalysts. The band gap was calculated from the UV-Vis spectra using the relationship $E = \frac{hc}{\lambda}$. The shift in the onset of absorbance has the effect of lowering the band gap by 0.4 electron volts from approximately 2.8 eV to 2.4 eV, which is in agreement with results obtained pseudo-plane wave density function modeling studies.[29]

Figure 2-2: The Fe-BTO characterization using (A) XRD indicating the crystalline nature of the thermally treated Fe-BTO and (B) the absorbance spectra of the (a) BTO and (b) Fe-BTO indicating a red-shift with Fe addition.
**Electrochemical impedance analysis:**

Electrochemical impedance spectroscopy (EIS) measurements offer insights into the effectiveness of the photocatalyst to separate the photogenerated charges. The EIS measurement was performed using the photocatalyst films prepared on conducting glass (ITO) in the presence of aqueous Na$_2$SO$_4$. A plot of the imaginary and real coordinates for the films in the presence and absence of photoillumination is shown in Figure 2-3. The greater the radius of the arc, the lower the extent of interfacial charge transfer occurring within the system.[35] A comparison of the Fe-BTO with the BTO indicates that the charge separation is greater with Fe_BTO than BTO attributable to the Fe presence. This improved charge separation can promote the photoactivity of the BTO. A similar observation was noted in earlier studies involving Fe doped TiO$_2$[35] and Fe doped graphitic C$_3$N$_4$[37].
Figure 2-3: The plot of the $Z_{\text{imag}}$ vs. $Z_{\text{real}}$ obtained using EIS measurements of the films made using BTO ($\Delta$, $\blacktriangle$) and Fe-BTO ($\nabla$, $\blacksquare$) in the absence of illumination (open triangles) and presence of illumination (closed triangles), are shown. The smaller radius of curvatures indicates better charge separation.

**Effects of Catalyst Loading:**

Figure 2-4 shows the effects of varying the loading of the photocatalyst in the slurry reactor. The optimal catalyst amount for the constant pressure batch reactor with an initial volume of 300 mL appears to be 150 mg. 200 mg of catalysts shows a 27% reduction in hydrogen production and a use of 250 mg shows a 58% reduction. An initial loading of 100 mg of catalyst shows a result similar to that of the 200 mg loading; a reduction in hydrogen production of 22%. It is thought that weight beyond 150 mg of catalyst contributes more to light scattering effects.
thereby lowering the amount of absorbed photons in the catalyst structure. The lower volume of hydrogen produced is attributable to the insufficient catalyst weight. Alternately, an amount less than 150 mg will not provide enough active sites for the given initial volume of reactants inside reactor of 300 mL for facilitating hydrogen generation.

Two aspects are clearly evident from these results. First, the hydrogen yield is noted to increase with time as shown in Figure 2-4B. The second is that hydrogen generation is faster after an initial incubation period of ~ 60 minutes. This 2-zone trajectory is indicated by marking them as I and II in Figure 2-4B. The hydrogen evolution can be attributable to the following steps: i) formation of the first intermediate HCHO, ii) photocatalysis of the HCHO to produce the second intermediate HCOOH and the hydrogen, and iii) formation of the CO₂ and additional hydrogen from the HCOOH. The reaction steps (Eqn. 2-1) include the formation of formic acid and formaldehyde have to be validated (this aspect is presented in the discussion section).

\[
Fe - BTO \xrightarrow{h_v} e_{cb}^- + h_{vb}^+
\]

\[
CH_3OH + 2h_{vb}^+ \rightarrow HCHO + 2[H^+]
\]

\[
2[H^+] + 2e_{cb}^- \rightarrow H_{2(g)}
\]

\[
HCHO + 2h_{vb}^+ + H_2O \rightarrow HCOOH + 2H^+
\]

\[
2H^+ + 2e_{cb}^- \rightarrow H_{2(g)}
\]

\[
HCOOH + 2h_{vb}^+ + 2e_{cb}^- \rightarrow CO_2 + H_{2(g)}
\]

**Overall Reaction**

\[
CH_3OH + H_2O \xrightarrow{6 \ h_v} CO_{2(g)} + 3H_{2(g)}
\]
Figure 2-4: The photocatalytic experiments performed using Fe-BTO of varying loading in the presence of a 250:50 (v/v) water: methanol mixture results in a (A) maximum in the cumulative hydrogen yield at a loading of 150 mg. (B) The time resolved hydrogen yield information indicates a presence of two distinct regions (I & II) where hydrogen generation rates differ, attributable to the intermediates.

Light Intensity Variation:

Figure 2-5A and 2-5B shows the effects of light intensity on the hydrogen yield from methanol water mixture. The light intensity was varied by wrapping the annulus in aluminum foil with different apertures (1 cm holes approximately 1 inch apart). This procedure had the effect of reducing light intensity from 100% to 61.7% and 31.7% (30000 lux to 20500 lux and 11500 lux). Reducing the light intensity showed a decrease in the production of hydrogen in the reactor. Hydrogen production was decreased by 59% at 20500 Lux. The fact that a very tiny amount of hydrogen was produced over the 130 minute experiment time at 10500 Lux indicates that reducing the intensity by 2/3rd causes complete stop in
photocatalysis. This suggests that the light (i) does not activate as many as e-h pairs, or (ii) the photogenerated charges are not significant enough to produce measurable quantities of hydrogen through the mechanism postulated earlier. This experiment indicates that intensity of the incident light plays a large part in the promotion of electrons from the valence band to the conduction band within the catalyst and all further experiments were performed with the intensity maintained at 30,000 lux. Similar observations have been reported using other photocatalysts such as, CdS and ZnS catalysts.[38]

**Figure 2-5:** (A) The hydrogen yield obtained from a 250:50 (v/v) water: methanol mixture using 150 mg of 1% Fe-BTO photocatalyst in the presence of a varying light intensity of (a) 30,000 lumens, (b) 20,000 lumens, and (c) 11,500 lumens is presented. (B) The time resolved hydrogen generation is presented and corresponds to the same conditions mentioned in Figure 5A.

**Catalyst Reusability:**

**Figure 2-6A and 2-6B** shows the effects of repeated use of the photocatalyst in multiple runs. The catalyst was cycled from one reaction to
another by removing all the residual solution after a 130 minute continuous run. The spent catalyst was collected by centrifugation, dried in an oven at a temperature of 120°C for 3 h and then re-used in the experiment by re-charging the reactor with the same initial reaction parameters (250 mL water, 50 mL of Methanol, 150 mg of catalyst). The reactor was again sufficiently purged with argon gas to remove any entrained gas species (18 minutes) and irradiated for 130 min under constant stirring.

The cycling of the catalyst in this manner showed a loss of hydrogen production; a reduction of 53.7% in the second cycle. A third cycling of the catalyst was performed after implementing the same steps as indicated above. The third cycle showed a further decrease of ~ 30% in hydrogen yield. Thus, there was a drop off in hydrogen production from the 1st catalyst cycle by 81.8%. These results indicate that some form of catalyst deactivation (poisoning) is occurring upon illumination of the catalyst in the water-methanol system which inhibits the hydrogen yield. Another interesting observation worth noting is that a significant color change (light yellow to dark gray) of the catalyst was observed over the 130 min reaction time after every experiment.
Figure 2-6: The photocatalytically obtained (A) cumulative hydrogen yield using 150 mg of Fe-BTO in the presence of a 250:50 (v/v) water: methanol mixture in three repeated use cycles is shown. The results in (A) and the time-resolved data in (B) indicate that the yield reduces from (a) 1\textsuperscript{st} cycle, to (b) 2\textsuperscript{nd} cycle, and (c) 3\textsuperscript{rd} cycle suggesting loss of photocatalytic activity.

III. Discussion

The preceding results indicate that i) an optimum loading of the Fe_BTO photocatalyst exists at 150 mg, beyond which photocatalytic hydrogen yield reduces, ii) the hydrogen generation follows a 2-zone trajectory, and iii) repeated use of the photocatalyst results in a substantial decrease in the hydrogen yield. This section presents the experiments performed and its analysis to further understand the reasons for these observations. The key aspects presented here are: (i) how much of the hydrogen is being produced from water and methanol oxidation, (ii) and what is the reason for the decrease in the hydrogen yield. The
observations on these experiments provide valuable insights into the two-zone hydrogen generation regions indicated in the time-resolved data.

**Deciphering the extent of hydrogen generation from the water–methanol mixture**

The effects of varying the methanol: water ratio on photocatalytic hydrogen generation is shown in Figure 2-7A and 2-7B. Keeping the 300 ml of mixture constant for every run, the reactor was charged with a methanol concentration of 4M, 8M, 12M, 16M, and 20M and hydrogen generation. The hydrogen evolved during the reaction increases linearly with an increasing methanol concentration reaching a maximum at the 20M concentration, an increase of approximately 2600%, indicating that the hydrogen yield is driven by the initial concentration of methanol. Similar observations are reported in the presence of other photocatalysts as well using methanol-water mixture. In the absence of methanol, no hydrogen evolution is detected confirming that H$_2$ evolution occurs via oxidation of methanol. As a comparison, pure BTO showed a hydrogen yield (<10%) in a 50:250 methanol-water mixture, which is less than Fe-BTO. The time-resolved hydrogen generation curve for each methanol-water ratio is shown in the Figure 2-7B. The two noteworthy aspects of this data are: i) hydrogen yield follow the same 2-zone trajectory regardless of the methanol concentration and ii) interestingly enough the duration of zone I appears to be reduced when the concentration of methanol is higher in the water-methanol mixture.
Figure 2-7. The (A) cumulative and (B) time-resolved hydrogen generated in the presence of (a) BTO (no Fe content) and (b-f) 1 % Fe-BTO with increasing methanol content is shown. The hydrogen yield was obtained from a water: methanol mixture composition (v/v) varying from (a,b) 250: 50, (c) 200:100, (d) 150:150, (e) 200:50, and (f) 50: 250.

Validation of mechanism through experiments using various additives:

In order to investigate the 2-zones further, hydrogen generation experiments were conducted, with the intermediates as additives: one each with formic acid and formaldehyde as the reacting species instead of methanol. The effects of the intermediates variation with the same initial parameters of 50:250 (v/v) is given in Figure 2-8A and 2-8B. The amount of hydrogen produced in order from smallest to largest is formaldehyde, then methanol, and finally formic acid. Formic acid shows an increase of 2000% in hydrogen production compared to when formaldehyde is used as the reactant. This result clearly indicates that the cause for the lag in the hydrogen generation lies in the intermediates and their ability to get oxidized to produce hydrogen. From a surface reaction standpoint the
key step is the transformation of formaldehyde to formic acid. Methanol exhibits higher hydrogen yield than formaldehyde due to the release of an additional molecule of H₂ during the first step in the mechanism.

Figure 2-8: The role of the different methanol photo-oxidation intermediates in the (A) cumulative hydrogen generation and the (B) time resolved hydrogen yield is reported. The focus was mainly on comparing (a) methanol with (b) formaldehyde and (c) formic acid at an initial concentration of 250:50 (v/v) water: intermediate mixture.

Thermodynamic properties of the intermediates also aid in clarifying the 2-zone process. The decomposition of formic acid is thermodynamically favorable (delta: \( \Delta H^{\circ}_{\text{rxn}} = -95.8 \text{ KJ/mol} \)) compared to that of methanol and formaldehyde (64.1 KJ/mol and 47.8KJ/mol respectively). This suggests that the increased hydrogen production rate in the presence of formic acid is attributable to the more oxidizability
of the molecule compared to the other participating species. On another note, formic acid and formaldehyde are classified as hazardous waste/model pollutant due to low flashpoint and corrosively limitations.[40] Hazardous wastes such as these are very costly to transport and dispose of, and are typically burned or otherwise destroyed in ways that have very negative effects to our atmosphere and environment. As this research shows, there is a potential to re-harvest the energy from these wastes for useful work in either a hydrogen fuel cell or hydrogen internal combustion engine. If the outlet stream of the reactor can also be combined with a carbon dioxide scrubber (in the form of a molecular sieve) perhaps hazardous waste disposal can be turned into a profitable enterprise. These results therefore, show the multi-functionality of the Fe-BTO photocatalysts as facilitators of a "waste-to-fuel" process (Scheme 2).
Scheme 2-2: The scheme summarizes the photooxidative conversion of methanol to CO\(_2\), intermediates, and eventually hydrogen. The specific intermediates that are expected to influence the hydrogen generation, are identified. The pathway for using BECONs such as Fe-BTO as photocatalyst in a “waste-to-fuel” process is illustrated.

Photocatalyst deactivation and recovery studies:

In order to understand, the reduction in the hydrogen yield, FTIR analysis of the reused catalyst was carried out. FTIR can be used to detect organic moieties on photocatalyst surface. The FTIR of the catalyst after use indicates new peaks at 2924, 2865 and 1726 cm\(^{-1}\), at the surface of the catalyst as shown in Figure 2-9A. These signals corresponds to the –OMe (methoxy) and –C=O (carbonyl) groups. These groups block the active sites on the surface, preventing/hindering the surface catalytic reactions from repeated cycles of the catalyst. Previously Mn_BTO (manganese modified BTO)[40] and TiO\(_2\)[41] catalysts showed similar attachment of carbonyl groups to the surface of the catalyst after reuse. This indicates the fact that the reaction is indeed occurring through a formaldehyde/formic acid path way generated from the hole mediated oxidation of the methanol as discussed earlier. These partly converted functional groups (as shown in Scheme 2) left at the active sites of the catalyst are the cause of the hydrogen production loss from one cycle to the next and a certain amount of regeneration time and/or processing may be necessary to maintain a consistent yield of hydrogen.

To test if regeneration of the photocatalyst is possible, an oxidative thermal treatment was considered. Since organic moieties are present on the surface, its
removal could help recover the catalyst. This oxidative treatment of the spent photocatalyst in air is expected to remove the organic moieties and recover the active sites of the catalyst surface.[42] The oxidative removal was performed by heating the spent catalyst in air at 350°C for a period of 8 h. The FTIR of the sample was performed and compared with the results of the pre-used Fe_BTO (pristine catalyst). After the heat treatment no aliphatic and carbonyl peaks could be detected using FTIR. Further, the UV-visible analysis (Figure 2-9B) of the heat treated catalyst and the pristine samples showed the same absorbance behavior. This indicates that there is no structural alternation after thermal treatment. These results indicate that the formation of the intermediates is the bottleneck to effective Fe_BTO photocatalyst performance but the catalyst can be regenerated using a simple oxidative thermal treatment.
Figure 2-9: The FTIR analysis of the pristine Fe-BTO, 3 times used Fe-BTO, and the regenerated Fe-BTO is shown in (A) indicating the formation of surface functionalities on the Fe-BTO after use. The binding of the functionalities as indicated in (B) is the basis for the steady decrease of the Fe-BTO photoactivity with subsequent cycles. Upon thermal treatment of the used photocatalyst (350°C, 8 hr, air), the photocatalyst recovers its surface features as indicated in the FTIR and absorbance spectra of (C).

Conclusion

This work provides a detailed insight into the functioning of a 1% Fe-bismuth titanate band gap engineering composite oxide nanostructure towards photocatalytic hydrogen generation. Catalyst loading, light intensity and methanol concentration - physicochemical factors that underline the performance of the photocatalyst - have been systematically investigated using a slurry-based reactor.
configuration. The time resolved hydrogen yield indicates the presence of a 2-zone trajectory with a slower hydrogen yield in zone I and a rapid boosting in hydrogen generation in zone 2. This response can be attributed to the variation in the oxidizability of the intermediates (Methanol $\rightarrow$ formaldehyde $\rightarrow$ formic acid $\rightarrow$ CO$_2$/H$_2$) produced during methanol oxidation. The fact that Fe-BTO demonstrates oxidative hydrogen generation from these molecules raises the tantalizing possibility that it could be a multifunctional photocatalyst driving photo-assisted waste-to-fuel conversion processes. Further, from a photocatalyst stability standpoint, repeated use indicates the formation of functional groups on the oxide surface as the cause for the continued reduction in the photocatalyst performance in subsequent cycles. A simple post-use oxidative treatment is effective in purging out these groups without imparting any detrimental transformation in the optical or physical features of the photocatalyst.
References

Chapter 1