NEW CATALYSTS FOR THE PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE TO C1 ORGANIC COMPOUNDS

by
Anna Kathryn Hailey

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Approved by

Advisor: Professor Wei-Yin Chen

Reader: Professor Nathan Hammer

Reader: Professor Carl Jensen

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ABSTRACT

ANNA KATHRYN HAILEY: New Catalysts for the Photocatalytic Reduction of Carbon Dioxide to C1 Organic Compounds
(under the direction of Wei-Yin Chen)

Photocatalytic reduction of carbon dioxide (CO_2) has recently been identified as one of the five notable research areas in catalysis because it simultaneously reduces carbon emissions while storing clean, “green” solar energy in organic compounds. The development of efficient photocatalysts that take advantage of solar radiation is therefore an important area of research. Titanium dioxide (TiO_2) is a commonly-used photocatalyst for this reaction, but it requires ultraviolet (UV) radiation to excite its electrons. Carbon-doping (C-doping) has been shown to reduce the intensity of energy required, thus allowing the photocatalyst to take advantage of the visible light spectrum. Copper (Cu), added as separated particles and not introduced into the catalyst structure, has also been reported to enhance the photocatalytic effect. Here, a comparison of the efficiency of CO_2 reduction by the following photocatalysts is reported: commercial TiO_2, commercial TiO_2-Cu, C-doped TiO_2, C-doped TiO_2-Cu, undoped TiO_2, and undoped TiO_2-Cu. Photocatalytic reactions were conducted in a single neck flask which was irradiated by a Xenon lamp. The aqueous product was analyzed for total organic carbon (TOC) content and also by using a mass spectrometer. Gas analysis was not conducted in the present study. Results suggest that among the photocatalysts studied here, commercial TiO_2 is the most effective in producing TOC. However, comparing only the samples synthesized from titanium sulfate ($TiOSO_4$) in our laboratory, C-doped TiO_2 is more effective than undoped TiO_2. The addition of copper was found to have an inconclusive effect on the production of TOC.

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LIST OF ABBREVIATIONS

C1	one carbon
$C_6H_{12}O_6$	glucose
$C_6H_5CH_3$	toluene
C-doped	carbon-doped
CH_2O	formaldehyde
CH_3OH	methanol
CO	carbon monoxide
CO_2	carbon dioxide
Cu	copper
GC	gas chromatograph
HCOOH	formic acid
MS	mass spectrometer
O_3	ozone
$Ti(SO_4)_2$	titanium sulfate
TiO_2	titanium dioxide
$TiOSO_4$	titanium sulfate
TOC	total organic carbon
UV	ultraviolet

1. INTRODUCTION

1.1. Impact of Energy and the Environment on National Security

The use of fossil fuels is both an energy security and climate change issue. Reliance on foreign energy costs countries both militarily and economically. The current global energy network lies perilously open to disruption, which would cause serious financial upheaval. (1) Examples of security threats include terrorist attacks on electricity grids and oil or gas pipelines and fuel supply restriction due to political disagreements. (2) In addition, the continued use of fossil fuels increases the production of CO_2 emissions. Over 24 billion metric tons of anthropogenic CO_2 emissions are released into the atmosphere each year. (3) This number is only expected to rise as developing countries increase power consumption to meet their growing economic demands. CO_2 consumption by the global chemical industry is holding steady at approximately 115 million metric tons per year, which is less than 1% of total production.

By trapping heat in the atmosphere, CO_2 is causing the Earth's temperature to slowly rise. Extreme weather, decrease in biodiversity, water shortages, desertification, and coastal erosion emerge as a few of the problems associated with climate change. In turn, these environmental problems will only increase issues of world hunger, infectious diseases, displaced populations, political instability, and civil unrest in already fragile areas. (1) Thus, the current reliance on foreign fossil fuels presents a twofold threat, challenging the national security of both developing and developed nations. (2)

1.2. Emerging Technological Solutions

Fortunately, renewable energy provides long-term solutions to both aspects of the energy security issue. Renewable energy resources (including solar energy, wind power, geothermal energy, hydropower, and biomass) provide clean, secure, and indigenous sources of power. Due to the constant variation of geographical environments, one single type of renewable energy is not likely to sufficiently support the energy needs of an entire nation; however, a diverse portfolio of renewable energy sources contributes to the flexibility, stability, and security of a country's energy system. The rich variety of energy supply reduces the disruptive impact of any one source, and local energy generation reduces the cost and improves the sustainability of production and transportation. Additionally, using renewable energy avoids the net production of CO_2 emissions into the atmosphere and thus reduces a country's impact on the environment and global climate change. Therefore, research, development, and implementation of renewable energy increasingly take a prominent role in political, economic, and environmental policy worldwide. (2)

Until an alternative energy infrastructure is developed worldwide, carbon capture and sequestration (CCS) technology has emerged as a short-term solution for the reduction of greenhouse gas emissions into the atmosphere. (4) However, current CCS technology faces serious issues, including the addition of a 25-35% energy penalty. One emerging carbon capture technique that utilizes alternative energy in order to reduce CO_2 emissions is the photocatalytic reduction of CO_2.

Solar energy is both renewable and abundant. In fact, the sun irradiates the earth with more energy per hour (4.3×10^{20} J) than humanity consumes in a year (4.1×10^{20} J). However, in 2001 less than 1.5% of the world's energy usage was from solar energy. (5) Therefore, there is a significant push to develop the technology to efficiently capture and store this energy to reduce the world's reliance on fossil fuels. The photocatalytic reduction of CO_2 is one such area of research. This technology was identified as one of the five notable research areas in catalysis because it simultaneously reduces carbon emissions while storing clean, green solar energy in organic compounds. (6)

1.3. Semiconductor Photocatalysis

Organic compounds have been produced via the photocatalytic reduction of CO_2 since 1921. (7) In the last forty years, there has been renewed interest in semiconductor photocatalysis due to its potential in environmental and solar energy applications. The photocatalytic property of semiconductors is related to their electronic structure - a filled valence band and an empty conduction band. (8) When a photon exceeding the semiconductor's band gap energy irradiates the semiconductor, it excites an electron from the valence band into the conduction band, creating a positively-charged electron hole. (8) This electron and electron hole pair is known as an exciton. Before the exciton decays (or, before the electron and electron hole recombine), it promotes the reaction of charged particles on the semiconductor's surface. (8) Of the semiconductors most commonly used in photocatalysis (such as TiO_2, SiO_2, CdS, WO_3, and Fe_2O_3), TiO_2 is the most significant due to several factors including its chemical inertness and commercial availability. (6) (8) (9)

The "band gap" is the energy difference between the valence band and the conduction band. Since the band gap of semiconductors can be high (for example, 3.2 eV for anataseTiO_2 (10), ultraviolet (UV) radiation is required to excite these electrons. As shown in Figure 1, UV radiation comprises only 3% of total solar radiation, so in terms of energy input, the efficiency of the photocatalytic reduction of CO_2 is low using solar irradiation. However, "doping" the semiconductor with nonmetal impurities such as carbon has been shown to reduce the band gap from the UV to the visible light region. (11) (12) This light absorption shift allows the doped semiconductor to utilize more of the abundant visible solar radiation.

The carbon-doping (C-doping) procedures developed by Raveendran et al (11) and Dong et al (12) are especially environmentally friendly. The Dong et al (12) process synthesizes anatase-phase mesoporous C-doped TiO_2 nanomaterials from inexpensive titanium sulfate ($Ti(SO_4)_2$) and glucose at low temperatures. This new method avoids the use of unstable or expensive precursors, treatment at high temperatures, and production of toxic byproducts associated with other doping processes. In their study, C-doped TiO_2 prepared by this method demonstrated a superior rate of photocatalytic decomposition of toluene ($C_6H_5CH_3$) when compared with that of undoped commercial-grade TiO_2 and C-doped TiO_2 prepared from high temperature oxidation of TiC. (12)

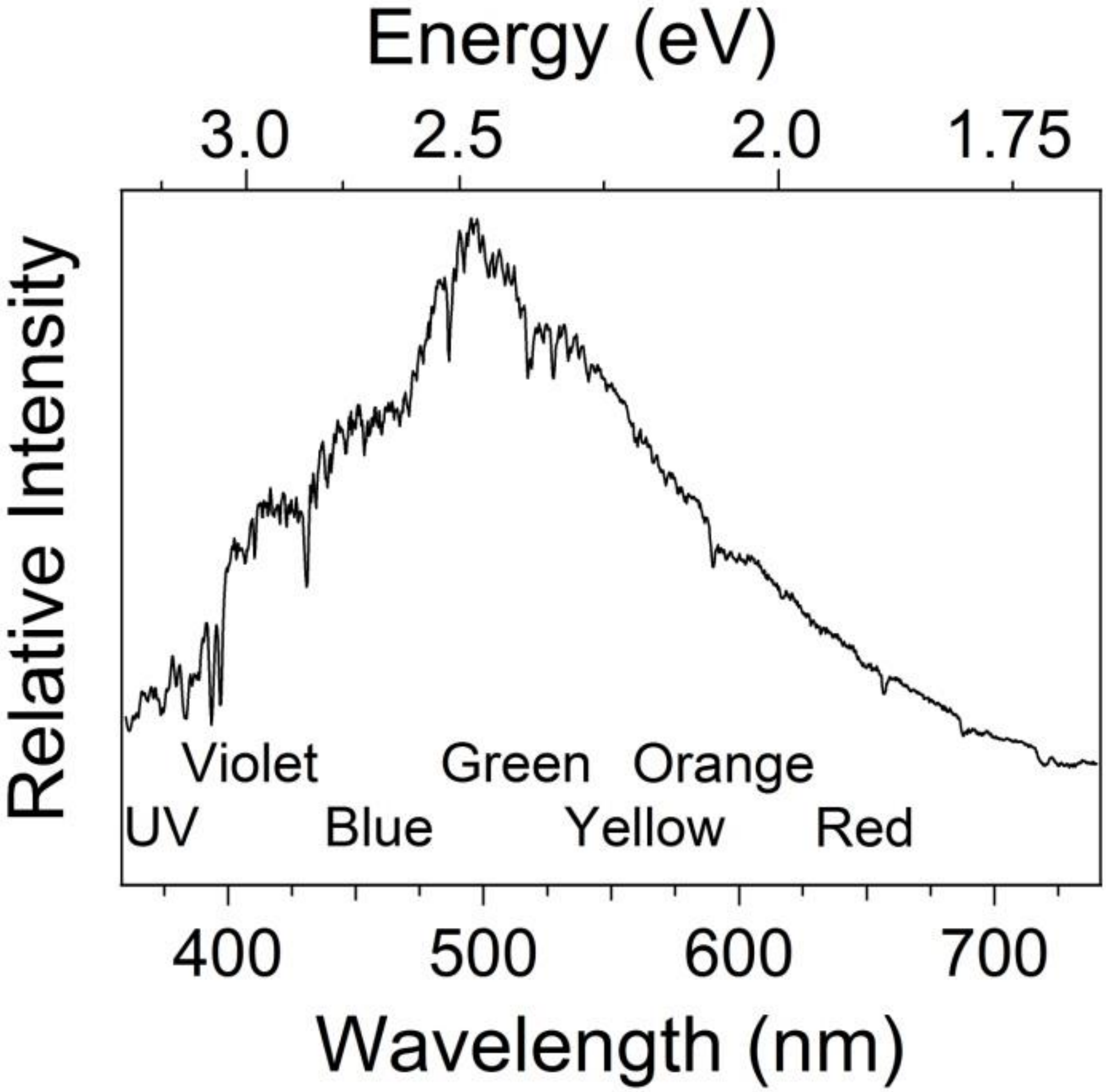

Figure 1. Solar emission spectrum obtained at the University of Mississippi. Dips in the spectrum are due to atmospheric gases such as CO_2, H_2O, and ozone (O_3).

1.4. TiO_2-photocatalyzed Reduction of CO_2 in Aqueous Solution

In the following reactions depicting the photocatalytic reduction of CO_2 in aqueous solution, titanium dioxide acts as the semiconductor and photocatalyst (13):

$$TiO_2 \overset{hv}{\rightarrow} {e_{cb}}^- + {h_{vb}}^+ \qquad (1)$$

oxidation: $${h_{vb}}^+ + (\mathrm{CH_3})_2\mathrm{CHOH} \rightarrow 2\mathrm{H}^+ + (\mathrm{CH_3})_2\mathrm{CO} \qquad (2)$$

reduction: $${e_{cb}}^- + CO_2 \rightarrow \ \dot{}CO_2^- \xrightarrow{H^+ + e^-} CO + OH^- \qquad (3)$$

$$CO + OH^- \xrightarrow{2H^+ + 2e^-} \ \dot{}C + H_2O \xrightarrow{2H^+ + 2e^-} \ \dot{}CH_2 \qquad (4)$$

$$\dot{}CH_2 \xrightarrow{2H^+ + 2e^-} \mathrm{CH_4} \qquad (5)$$

Upon irradiation with light of an adequate frequency, electrons are excited to a higher energy level. The small molecules CO_2 and H_2O attack the charged sites caused by the exciton to form C1 organic compounds as shown in Figure 2. (9) (14)

In 1992, Hirano et al (15) demonstrated the photocatalytic reduction of CO_2 in aqueous solution by UV irradiation, with TiO_2 and Cu powder acting as co-catalysts for the reaction. Their method produced the organic compounds CH_2O (formaldehyde), methanol (CH_3OH), and formic acid (HCOOH) in the liquid phase and carbon monoxide (CO) in the gas phase. Since no product was formed without the addition of Cu as a co-catalyst, this suggested that TiO_2 was insufficient to photocatalyze the reaction on its own. In 1994, Ohta et al (16) demonstrated the photocatalytic conversion of aqueous solutions of CO_2 irradiated by sunlight and catalyzed by silicate rocks, producing H_2 and CH_4. In

2000, Ohta et al (17) further demonstrated the abiological formation of HCOOH on common rocks found in nature. It was found that a reaction time greater than nine hours caused the secondary decomposition of the organic compounds into CO_2 and H_2.

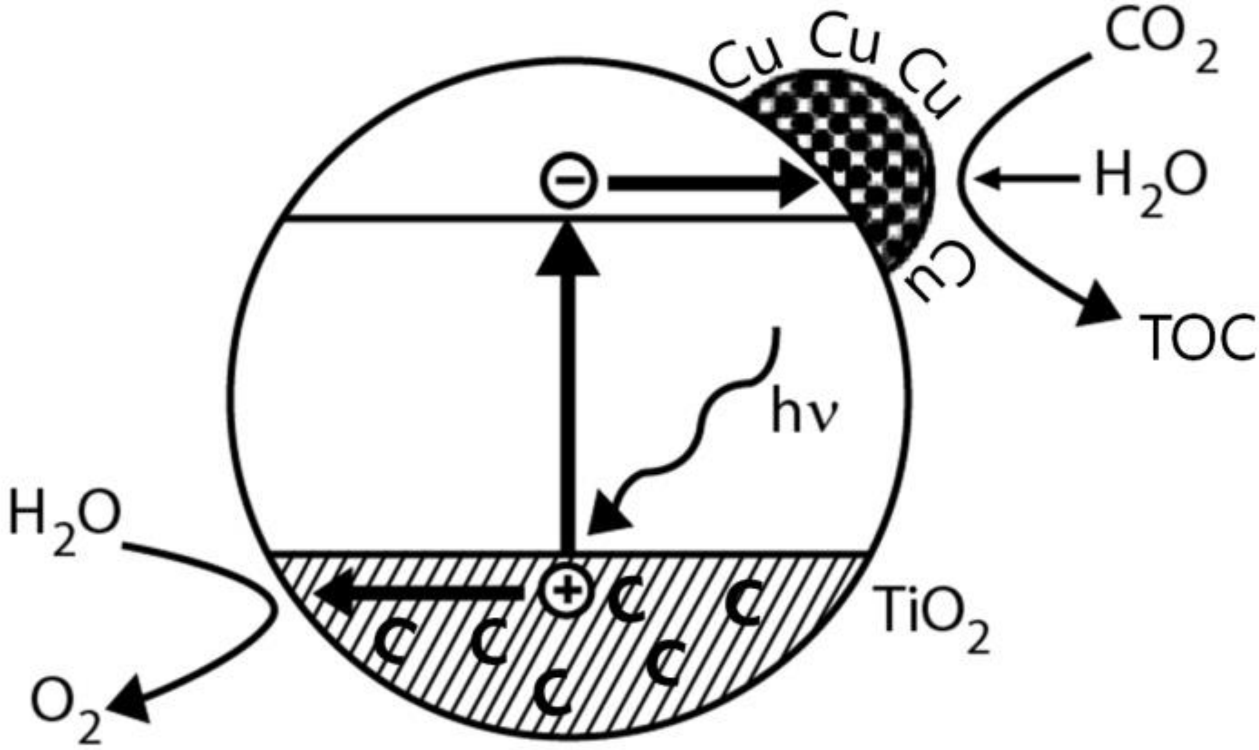

Figure 2. TiO_2 catalyzes the photochemical conversion of CO_2 to organic compounds while Cu and carbon-doping enhance the process through electron transfer and band gap reduction. (9) (14)

2. OVERVIEW OF THE EXPERIMENT

The specific goals of the current work can be summarized as follows:

- To compare the effectiveness of C-doped and undoped TiO_2 produced by a comparable procedure,
- To compare the effectiveness of $TiOSO_4$-based and commercial TiO_2, and
- To investigate the effectiveness of Cu as a co-catalyst.

The incentives for achieving these goals are discussed in the subsequent subsections.

2.1. C-doped TiO_2 vs. undoped TiO_2

Nonmetal doping of semiconductors has been shown to reduce the band gap to allow for greater use of visible light radiation. The synthesis method developed by Dong et al (12) is useful for preparing catalysts with which to compare the effect of doping. This is because the same low-temperature process can be used to produce both C-doped TiO_2 and undoped TiO_2. (The production of C-doped TiO_2 merely requires one additional, inexpensive ingredient – glucose). Thus, it is possible to create catalysts with the same level of purity in order to more accurately determine the effect of doping. Since C-doped TiO_2 prepared by this method demonstrated a superior rate of photocatalytic decomposition of $C_6H_5CH_3$, it is also expected to exhibit a greater rate of photocatalytic reduction of CO_2.

2.2. $TiOSO_4$-based TiO_2 vs. commercial TiO_2

Although high-purity TiO_2 is readily available, it is commercially produced via sol-gel synthesis. This high-temperature process consumes a great amount of energy; thus, the amount of CO_2 removed from the atmosphere by a commercial-TiO_2 photocatalyst is counterbalanced by the amount of CO_2 produced in the synthesis of the photocatalyst itself. If an effective TiO_2 photocatalyst can be synthesized from a low energy-impact method, the cost and energy savings could be significant. Thus, the results from TiO_2 synthesized from the environmentally-friendly method developed by Dong et al (12) will be compared to those of commercial TiO_2. Titanium sulfate in the form of $TiOSO_4$ is substituted here, however, for $Ti(SO_4)_2$, since $Ti(SO_4)_2$ is not readily available.

2.3. Effect of Cu as a co-catalyst

Previous studies have suggested that mixing Cu power into TiO_2 suspensions promotes the photocatalytic reaction of CO_2 to C1 organic compounds. Hirano et al (15) proposed that this effect is due to the excited electron rapidly transferring to the Cu particles, thereby increasing the longevity of the exciton. Thus, Cu would promote the reaction by separating the sites of reduction and oxidation and increasing the amount of time available for molecular interaction at these sites before the electron and electron-hole recombine. It is expected that TiO_2 samples with Cu powders added to act as a co-catalyst will have an enhanced rate of photocatalytic efficiency similar to that observed by Hirano et al. (15)

2.4. Experimental Parameters

In order to complete these three investigations, the efficiency of CO_2 reduction of the following catalysts was observed:

- commercial TiO_2
- commercial TiO_2-Cu
- C-doped TiO_2
- C-doped TiO_2-Cu
- undoped TiO_2 (synthesized from $TiOSO_4$)
- undoped TiO_2-Cu (synthesized from $TiOSO_4$)

The efficiency of CO_2 reduction was determined by the amount of total organic carbons (TOC) produced. Additional samples without catalyst (containing only CO_2-H_2O and only H_2O) were run through the experimental procedure in order to determine how much total organic carbon (TOC) occurs naturally in these systems. Following sample preparation, an irradiation method adapted from Hirano et al (15) was followed. A Xenon arc lamp was employed to induce the photochemical reaction because it efficiently mimics the solar emission spectrum. Slight variations to the Hirano et al (15) method include the scale of the photocatalytic cell and the power of the light source.

3. MATERIALS AND METHODS

3.1. Synthesis of Doped and Undoped TiO_2

To synthesize C-doped TiO_2, glucose (99.9% $C_6H_{12}O_6$, CAS#50-99-7**)** and titanium sulfate ($TiOSO_4 \times H_2O$, CAS#13693-11-3) are mixed in a 1:50 molar ratio with 700 mL of distilled water in a 1 L stainless steel cylinder. The cylinder is then hydrothermally treated in a vacuum oven (VWR Model 1410) at 160 ºC for twelve hours. After heating, the product is filtered, washed three times with distilled water, and dried in the vacuum oven at 60 ºC to obtain C-doped TiO_2. Undoped TiO_2 is prepared in a similar fashion without the addition of glucose.

3.2. Photochemical Reaction Procedure

250 mL of distilled water is added to a 500 mL Ace Glass single neck flask with a stopcock septum port side arm. A dip tube extends to the bottom of the flask. 2.5 g of a TiO_2 sample (C-doped, undoped, or commercial) is added to a flask. To some samples, 1.5 g Cu powders (GFS Chemicals, <0.044 mm diameter) are also added. Instrument grade CO_2 (>99.99%) is bubbled through the aqueous solution at 50 mL/min for one hour.

The flask is then placed in a sonicator (Fisher Scientific FS30H) and irradiated by a 450 W Edinburgh Instruments Xenon 900 Lamp for nine hours (see Figures 3 and 4). The beam of Xenon light activates the photocatalytic reaction to convert CO_2 to organic compounds. Water is continually added to the sonicator to replace that which is lost by evaporation and also to keep the water temperature between 40 to 60 ºC.

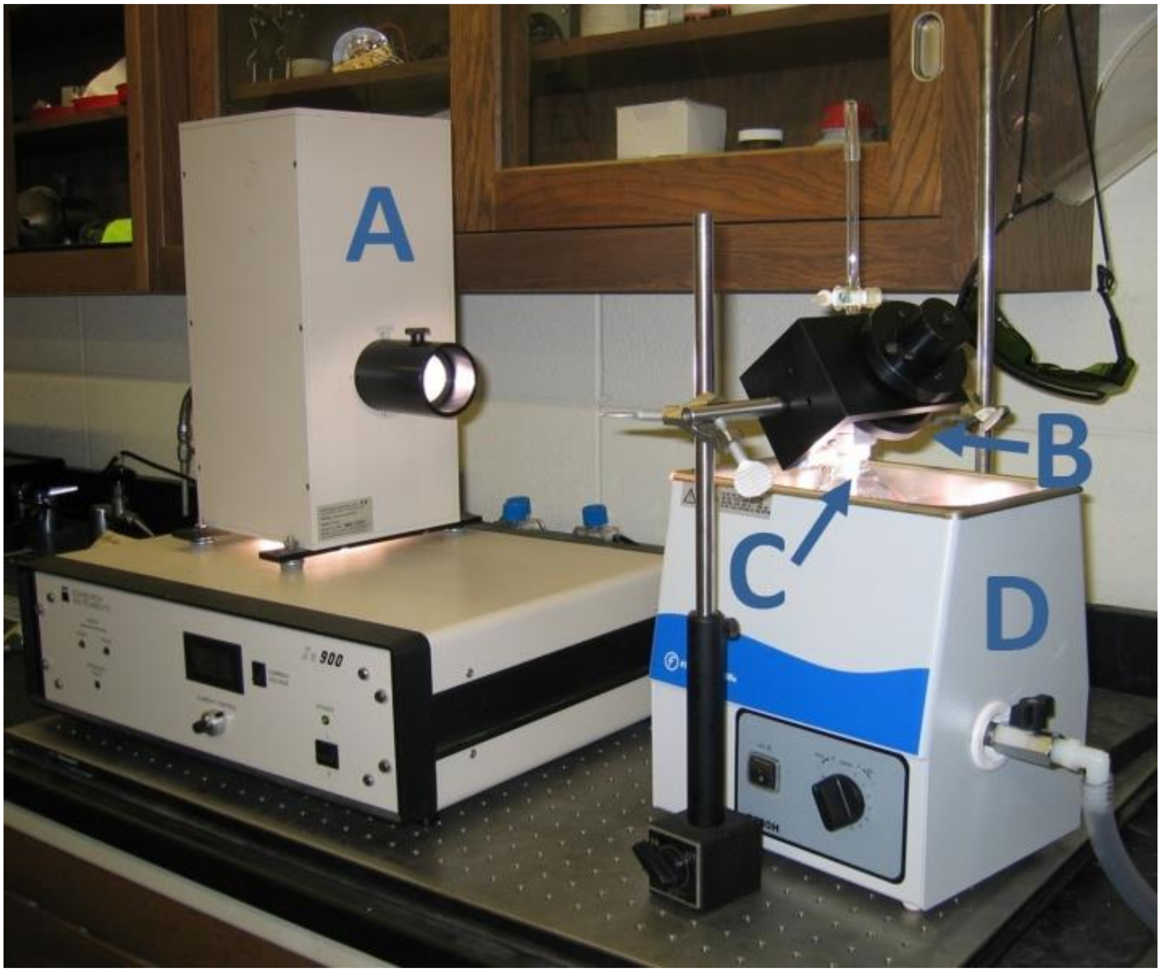

Figure 3. Apparatus for photocatalysis with the Xenon lamp. The light from the 450 W Xenon lamp (A) shines onto a mirror (B), which reflects the beam onto the solution in the flask (C) in the sonicator (D).

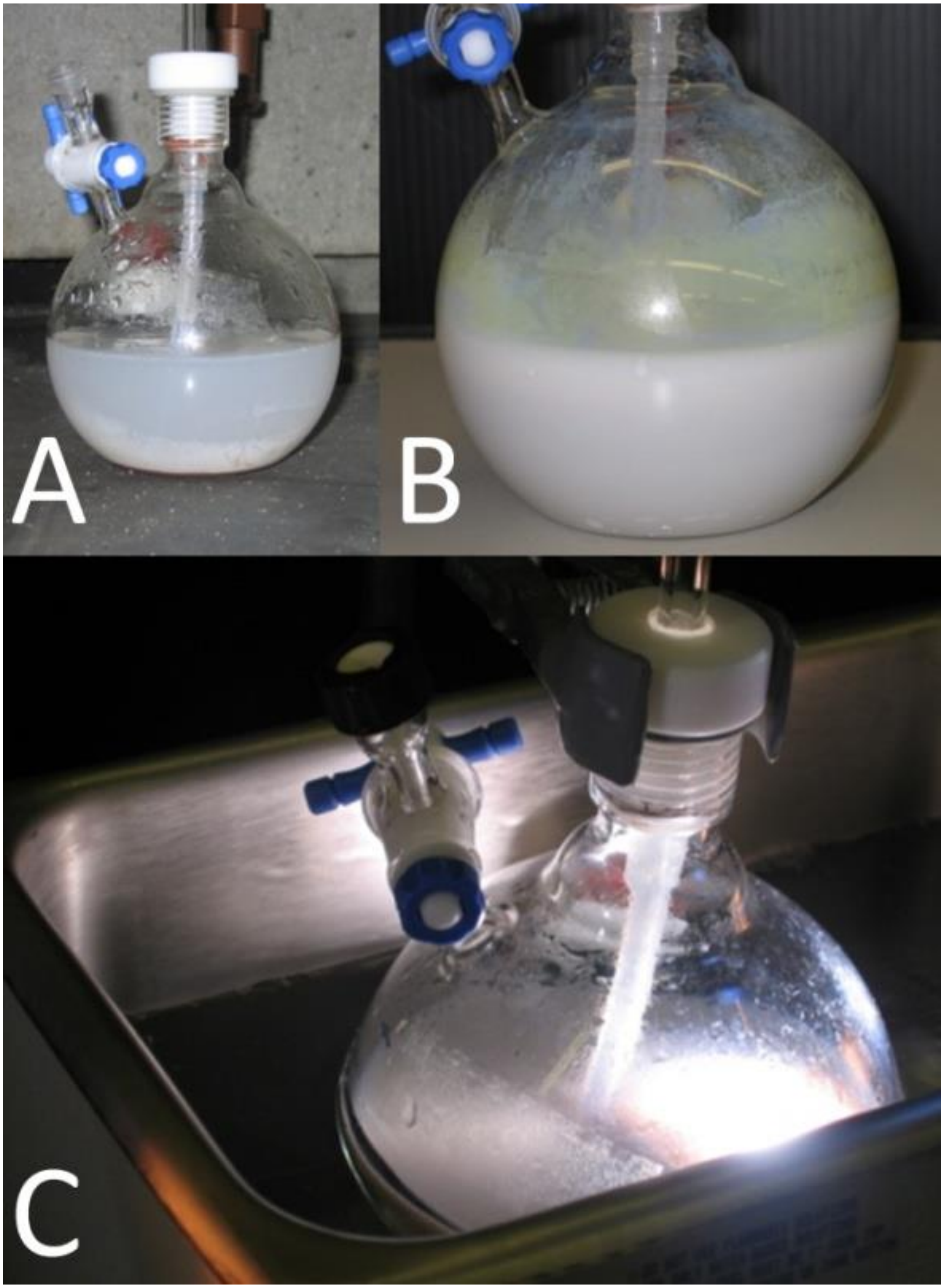

***Figure 4**.* Sample of TiO_2 (A) before, (B) after, and (C) during photo-catalysis. The yellow-green coating produced on the flask suggests the formation of organic compounds.

3.3. Analysis Procedure

After irradiation, the gaseous products are released from the flasks through the stopcock. Analysis of the gaseous products is not conducted in this study. The milky aqueous products are centrifuged (Fisher Scientific Micro Centrifuge Model 235C) and then filtered to obtain a clear aqueous solution. These solutions are analyzed by a gas chromatograph (Agilent Technologies 6890) / 5973N mass spectrometer (GC/MS). The GC oven is maintained at 140 ºC. The sample analysis is repeated twice to ensure reproducibility.

To measure TOC content, the aqueous samples were sent to Huffman Laboratories for TOC analysis by SM 5310 C. This is a UV/persulfate oxidation method that utilizes sodium persulfate as an oxidant and either heat or UV radiation to activate the reagents. (18)

To determine the specific identities of the organic compounds produced, the aqueous samples were further analyzed at the University of Mississippi. This analysis included the experiment samples as well as a standard solution of CH_2O (which contains both H_2O and CH_3OH to stabilize the solution). According to the MS results, there was no significant amount of HCOOH and CH_3OH in the experimental products (indicated by the lack of peaks at their characteristic positive ion mass signatures of 45 and 31, due to $HCOO^+$ and CH_3O^+, respectively.) Thus, quantification has focused on CH_2O, which is the major product (almost 40% of the TOC produced). CH_2O has a characteristic positive ion mass signature of 29 due to CHO^+. However, mass 29 in the spectrum of the CH_2O standard is contributed by CH_2O, $CH_3OCH_2OCH_3$, and $HOCH_2OCH_3$, these last two molecules being the products of reactions between CH_2O and CH_3OH. (19) (20) (21) Thus, the calibration value of CH_2O is underestimated if mass 29 of the standard is used as the characteristic mass. The maximum possible error (occurring if all CH_3OH completely converted to $HOCH_2OCH_2$ and did not contribute to mass 29) would yield a 30% underestimated CH_2O calibration value, or a 30% overestimated CH_2O yield in the experimental results. Thus, the reported CH_2O yields from experimentation are estimated from the amount present in the standard solution based on an adjusted calibration value. (19) (20) (21) Figure 5 presents the total ion and mass 29 chromatograms of two injections and the MS spectrum of one commercial-TiO_2-CO_2-H_2O sample.

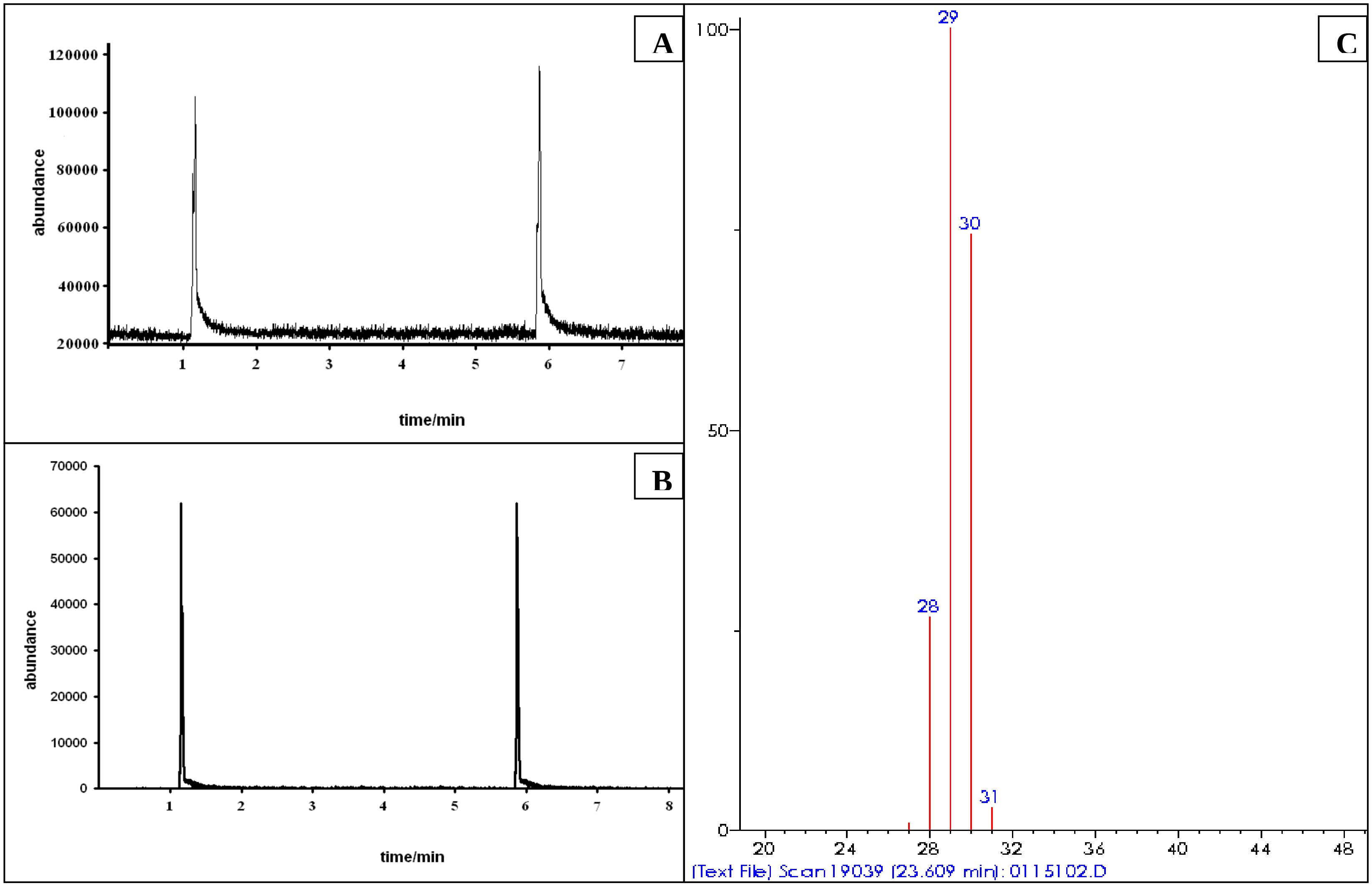

Figure 5. Chromatograms and Spectrum of a TiO_2-CO_2-H_2O Sample. This figure shows the total ion chromatogram (2 consecutive injections) (A), mass 29 chromatogram (2 consecutive injections) (B), and MS spectrum (C).

4. RESULTS

4.1. C-doped TiO_2 vs. undoped TiO_2

The photocatalytic activity of C-doped TiO_2 is in fact greater than that of undoped TiO_2, both with and without Cu (see Table 1). The amount of CH_2O produced by C-doped TiO_2 is 53% greater than that of undoped TiO_2, and the amount of TOC produced by C-doped TiO_2 is 164% greater than that of undoped TiO_2. In addition, the amount of CH_2O produced by C-doped TiO_2-Cu is 358% greater than that of undoped TiO_2-Cu, and the amount of TOC produced by C-doped TiO_2-Cu is 77% greater than that of undoped TiO_2-Cu. This discovery is significant because the C-doping procedure of Dong et al (12) as used here is inexpensive, does not require high temperatures, and does not produce toxic materials. Thus, this procedure reduces the amount of CO_2 produced in the photocatalyst synthesis process while increasing the amount of CO_2 consumed in the photocatalytic reaction process.

4.2. $TiOSO_4$-based TiO_2 vs. Commercial TiO_2

The photocatalytic activity of undoped commercial-grade TiO_2 is greater than that of both doped and undoped $TiOSO_4$-based TiO_2, both with and without Cu. The amount of CH_2O produced by commercial-grade TiO_2 is 34% greater than that of C-doped TiO_2-Cu, 515% greater than undoped TiO_2-Cu, 1154% greater than C-doped TiO_2, and 1820% greater than undoped TiO_2. The amount of TOC produced by commercial-grade TiO_2 is

55% greater than that of C-doped TiO_2-Cu, 175% greater than undoped TiO_2-Cu, 217% greater than C-doped TiO_2, and 738% greater than undoped TiO_2.

The $TiOSO_4$ used in these experiments was low grade (65% purity); if higher purity $TiOSO_4$ were to be used, it is likely that TOC and CH_2O production from the $TiOSO_4$-based catalysts would be even greater. Whether or not the $TiOSO_4$-based catalysts reach the effectiveness of the commercial-grade ones, the benefit to using $TiOSO_4$-based TiO_2 is that its synthesis process is a low temperature and thus low energy impact method, both relatively inexpensive and environmentally-friendly.

4.3. Effect of Cu as a Co-Catalyst

The effect of the Cu powder on the photocatalytic efficiency of doped and undoped TiO_2 was found to be inconclusive. While the TOC for undoped TiO_2 was greater with Cu than without (2.05 mg/L vs 1.42 mg/L), this trend was reversed for the C-doped TiO_2 (3.62 mg/L with Cu vs. 3.74 mg/L without) and the commercial TiO_2 (5.62 mg/L with Cu vs. 11.9 mg/L without). Furthermore, while the amount of CH_2O produced by C-doped TiO_2 was greater with Cu than without (0.176 mg/L vs 0.0929 mg/L), this trend was reversed for the undoped TiO_2 (0.0383 mg/L with Cu vs. 0.0607 mg/L without) and the commercial TiO_2 (0.236 mg/L with Cu vs. 1.17 mg/L without).

These results suggest that Cu may not be necessary as a co-catalyst for all photocatalytic reaction systems. The different results may stem from the modifications to the Hirano et al (15) method made for this study. The higher temperatures achieved during this study (62-66 °C vs. 40 °C for Hirano) enhance the conversion rate of CO_2 regardless of the addition of Cu. This perhaps masks the contribution of Cu observable at lower temperatures. Another possible factor is that the Cu powder may obstruct light from reaching the TiO_2, thus reducing Cu's positive effect on the photocatalytic efficiency. Yet an additional explanation perhaps results from the state of the Cu particles. Both in the Hirano et al (15) study and the experiment presented here, the Cu particles are separate from the TiO_2. It is possible that actually doping the Cu into the TiO_2 would produce a stronger positive effect on photocatalysis than simply mixing the Cu and TiO_2 particles together.

Table 1. Summary of Experimental Parameters and Statistical Analyses. Experimental data obtained at the University of Mississippi, with the results of Hirano et al (15) shown as reference. Each photocatalyst was tested three times to ensure reproducibility of results.

Experiment	**Reactants**	**Amount of Water**	**Purity of CO_2**	**TiO_2**	**Cu Powder**	**Experiment Setup**	**Light Source**	**Temp., °C**	**TOC, mg/L**	**Avg. TOC, mg/L**	**Standard Deviation, mg/L**	**Carbon as CH_2O, mg/L**	**Avg. Carbon as CH_2O, mg/L**	**Standard Deviation, mg/L**
Hirano et al (15)	TiO_2-Cu-CO_2-H_2O	30 mL Millipore Water	99.99%	0.500 g 99.99% Anatase	0.300 g 99.9%	Cylindrical Pyrex Cell (60 mL)	500 W Xenon Lamp (WAKOM KXL-500F)	40	2.40†			0.800		
1	Commercial TiO_2-CO_2-H_2O	250 mL Distilled Water	>99.99%	2.50 g 99.9% Inframat Advanced Materials Anatase		ACE Glass Inc. 6934-27 Flask (500 mL)	450 W Edinburgh Instruments Xenon 900 Lamp	Avg. 65	11.9	11.9	0.751	1.26	1.17	0.134
2	Commercial TiO_2-CO_2-H_2O								11.1			1.07		
3	Commercial TiO_2-CO_2-H_2O								12.6			0.654*		
4	Commercial TiO_2-Cu-CO_2-H_2O				1.50 g 99%			Avg. 66	5.99	5.6	0.738	0.165	0.236	0.112
5	Commercial TiO_2-Cu-CO_2-H_2O								4.77			0.177		
6	Commercial TiO_2-Cu-CO_2-H_2O								6.10			0.365		
7	CO_2-H_2O							Avg. 62	1.11	0.567	0.472	ND**	--	--
8	CO_2-H_2O								0.260			ND**		
9	CO_2-H_2O								0.330			ND**		
10	Distilled Water								0.640					

Table 1 continued.

Experiment	Reactants	Amount of Water	Purity of CO_2	TiO_2	Cu Powder	Experiment Setup	Light Source	Temp., °C	TOC, mg/L	Avg. TOC, mg/L	Standard Deviation, mg/L	Carbon as CH_2O, mg/L	Avg. Carbon as CH_2O, mg/L	Standard Deviation, mg/L
11	undoped TiO_2-CO_2-H_2O	250 mL Distilled Water	>99.99%	GFS Chemicals 65% $TiOSO_4$		ACE Glass Inc. 6934-27 Flask (500 mL)	450 W Edinburgh Instruments Xenon 900 Lamp	Avg. 65	1.71	1.42	0.311	0.0646	0.0607	0.0109
12	undoped TiO_2-CO_2-H_2O								1.45			0.0691		
13	undoped TiO_2-CO_2-H_2O								1.09			0.0483		
14	undoped TiO_2-Cu-CO_2-H_2O				1.50 g 99%				1.49	2.05	0.605	0.0487	0.0383	0.009
15	undoped TiO_2-Cu-CO_2-H_2O								2.69			0.0354		
16	undoped TiO_2-Cu-CO_2-H_2O								1.96			0.0309		
17	C-doped TiO_2-CO_2-H_2O			GFS Chemicals 65% $TiOSO_4$ & 99.9% Anhydrous Glucose in 1:50 Molar Ratio				Avg. 63	3.26	3.74	0.525	0.0928	0.0929	0.0191
18	C-doped TiO_2-CO_2-H_2O								4.30			0.0738		
19	C-doped TiO_2-CO_2-H_2O								3.66			0.112		
20	C-doped TiO_2-Cu-CO_2-H_2O				1.50 g 99%				3.32	3.62	0.260	0.242	0.176	0.107
21	C-doped TiO_2-Cu-CO_2-H_2O								3.76			0.233		
22	C-doped TiO_2-Cu-CO_2-H_2O								3.78			0.0516		

Notes: All experiments, including those by Hirano et al (15),were conducted with 9 hours of reaction time.

** Not detectable.

† TOC from Hirano et al (15) was calculated from peak product formations of aqueous organic compounds including methanol, formaldehyde, and formic acid.

5. CONCLUSIONS

Based on the preceding data, the following conclusions can be drawn:

- Commercial TiO_2 is a more effective photocatalyst than either C-doped or undoped TiO_2 synthesized from $TiOSO_4$.
- C-doped TiO_2 is a more effective photocatalyst than undoped TiO_2.
- Cu serves as a co-catalyst for some photocatalytic systems

Further research could explore several different areas of this experiment. More results data could be collected by analyzing the composition of the gaseous products with a GC column, perhaps by using isotopically labeled CO_2. Additionally, this analysis will be necessary to close the material balance. The CH_2O quantification method could be made more precise, since the standard deviation for the CH_2O result calculation was often found to be of the same order of magnitude as the actual quantity. In order to more clearly determine the effect of Cu as a co-catalyst, the size and amount of Cu powder and the average operating temperature could be varied in additional experiments. Cu could also be doped into the TiO_2, in order to compare this effect to that of Cu as a separate particle from the TiO_2.

Dong et al (12) tested the photocatalytic activity of C-doped TiO_2 prepared with three different molar ratios of $C_6H_{12}O_6$ to $Ti(SO_4)_2$: 3:50 (high concentration), 1:50 (middle concentration), and 1:150 (low concentration). Since Dong et al (12) found that the middle concentration C-doped TiO_2 yields the maximum photocatalytic activity, this was the concentration adopted for the experiment detailed here. Although high concentration C-doped TiO_2 has the lowest band gap (2.78 eV), any increased photocatalytic activity is suppressed by the additional carbon atoms causing oxygen vacancies to populate the impurity states. However, a more ideal ratio might exist between the 1:50 and 3:50 $C_6H_{12}O_6$ to $TiOSO_4/Ti(SO_4)_2$ concentrations. Future work could include finding the amount of carbon doping that optimally enhances photocatalytic activity.

LIST OF REFERENCES

1. Finel, B. *Climate Security Index.* s.l. : American Security Project, 2009.
2. Olz, S. *Contribution of Renewables to Energy Security.* Paris : International Energy Agency, 2007.
3. Intergovernmental Panel on Climate Change. *Climate change 2007 - The physical science basis: Working group I contribution to the fourth assessment of the IPCC.* Cambridge : Cambridge University Press, 2007a.
4. Gore, A. *Our Choice: A plan to solve the climate crisis.* Emmaus, PA : Rodale Books, 2009.
5. Lewis, N.S. and G. Crabtree. *Basic research needs for solar energy utilization.* Washington, DC : Office of Basic Energy Science, US Department of Energy, 2005.
6. Bell, A.T., B.C. Gates, and D. Ray. *Basic research needs: catalysis for energy.* Washington, DC : Office of Basic Energy Science, US Department of Energy, 2007.
7. Baly, E.C.C., I.M. Heilbron, and W.F. Barker. *The synthesis of formaldeyde and carbohydrates from carbon dioxide and water.* 119, 1921, J. Chem. Soc., pp. 1025-1035.
8. Hu, X., G. Li, and J.C. Yu. *Design, Fabrication, and Modification of Nanostructured Semiconductor Materials for Environmental and Energy Applications.* 5, 2010, Langmuir, Vol. 26, pp. 3031-3039.
9. de Lasa, H., B. Serrano, and M. Salaices. *Photocatalytic reaction engineering.* New York, NY : Springer, 2005.
10. Graham, J.D. and N.I. Hammer. *Photocatalytic water splitting and carbon dioxide reduction.* s.l. : Springer, 2012, Handbook of Climate Change Mitigation.

11. Raveendran, P., J. Fu, and S.L. Wallen. *Completely "green" synthesis and stabilization of metal nanoparticles.* 125, 2003, J. Am. Chem. Soc.

12. Dong, F., H. Wang, and Z. Wu. *One-step "green" synthetic approach for mesoporous C-doped titanium dioxide with efficient visible light photocatalytic activity.* 113, 2009, J. Phys. Chem. C, pp. 16717-16723.

13. Palmisano, G., V. Augugliaro, M. Pagliarob, and L. Palmisano. *Photocatalysis: A promising route for 21st century organic chemistry.* 33, 2007, Chemical Comminucations, pp. 3425-3437.

14. Linsebigler, A., G. Lu, and J.T. Yates Jr. *Photocatalysis on TiOn surfaces: Principles, mechanisms, and selected results.* 95, 1995, Chemical Reviews, pp. 735-758.

15. Hirano, K., K. Inoue, and T. Yatsu. *Photocatalysed reduction of CO2 in aqueous TiO2 suspension mixed with copper power.* 1992, J. Photochem. Photobiol. A: Chem., Vol. 64, pp. 255-258.

16. Ohta, K., T. Kawamura, S. Kuroda, and T. Mizuno. *Photocatalytic reduction of CO2 by silicate rock sands under sunlight irradiation.* Tsu, Japan : Electrochem. Society, 1994. Symp. of Env. Aspects of Electrochem. and Photoelectrochem.

17. Ohta, K., H. Ogawa, and T. Mizuno. *Abiological formation of formic acid on rocks in nature.* 2000, Applied Geochemistry, Vol. 15, pp. 91-95.

18. Visco, G., L. Campanella, and Nobili, V. The international norm for the measure of the TOC and the carbons in waters chronological and critical analysis. [Online] 2003. http://w3.uniroma1.it/chemo/congress/veneziatoc/poster_veneziaA0.pdf.

19. Gold, A., D.F. Utterback, and D.S. Millington. *Quantitative analysis of gas-phase formaldehyde molecular species at equilibrium with formalin solution.* 1984, Ana. Chem., Vol. 56, pp. 2879-2882.

20. Albert, M., B.C. Garcia, C. Kuhnert, R. Peschla, and G. Maurer. *Vapor-liquid equilibrium of aqueous solutions of formaldehyde and methanol.* 8, 2000, AIChE Journal, Vol. 46, pp. 1676-1687.

21. Hasse, H., M. Schmitt, and M. Ott. *Reaction kinetics of the systems formaldehyde-water-methanol and hexyl acetate.* s.l. : Intelligent Column Internals for Reactive Separations, 2001.

22. Chen, W.Y., J. Seiner, T. Suzuki, and M. Lackner (Ed.). *Handbook of climate change mitigation.* s.l. : Springer, 2012.

APPENDICES

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A.1. CISS CAPSTONE SUMMARY

Problem

The use of fossil fuels is both an energy security and climate change issue. The United States oil supply relies heavily on fuel purchased from foreign sources. Many of these countries are economically and politically unstable, and their diplomatic relations with the United States are tenuous at best. Additionally, during transportation from these foreign countries to United States oil, the fuel (traveling in pipelines, tankers, etc) lies open to attack. A major economic, political, or diplomatic disturbance or terrorist attack cutting off access to the fuel supply could cause serious financial upheaval in the United States. In addition, the continued use of fossil fuels increases the production of CO_2 emissions. By trapping heat in the atmosphere, CO_2 is causing the Earth's temperature to slowly rise. Extreme weather, water shortages, desertification, and coastal erosion emerge as a few of the problems associated with climate change. In turn, these environmental problems will only increase issues of world hunger, displaced populations, political instability, and civil unrest in already fragile areas. Fortunately, renewable energy technologies provide long-term solutions to both the energy security and climate change issues. Renewable energy resources (including solar energy, wind power, geothermal energy, hydropower, and biomass) are indigenous sources of power that do not produce pollutants or CO_2 emissions.

Solution

Therefore, use of these resources can reduce the United States' reliance on foreign sources of oil, as well as reducing the United States' impact on the environment. Until the use of renewable energy technologies is developed worldwide, carbon capture and sequestration (CCS) technology has emerged as a short-term solution for the reduction of greenhouse gas emissions into the atmosphere.

One emerging carbon sequestration technique that utilizes renewable energy in order to reduce CO_2 emissions is the photocatalytic reduction of CO_2. In the results presented in this paper, it is shown that an inexpensive, easy-to-produce, and environmentally-friendly photocatalyst (C-doped TiO_2) can effectively use renewable solar energy to remove CO_2 from aqueous solutions. Due to the environmental implications of this technique's successful ability to sequester CO_2 in organic compounds, the research, development, and implementation of this technique should take a significant role in political, economic, and environmental policy worldwide.

Facts and Evidence

In this reaction, CO_2 reacts with H_2O to produce C1 (one carbon) organic compounds such as CH_2O (formaldehyde), methanol (CH_3OH), and formic acid ($HCOOH$). "Reduction" refers to the fact that the oxidation state of the carbon is reduced from +4 in CO_2 to +2 to -2 in these organic compounds. "Photocatalytic reduction" refers to the fact that, on its own, CO_2 is too stable to react with H_2O, and therefore a photocatalyst is needed for this reaction to take place. When light strikes a photocatalyst, it absorbs the light's energy. This excess energy causes the photocatalyst's electrons to become "excited" and jump to a higher energy level, leaving behind electron holes. After releasing the excess energy at the higher energy level, the electrons fall back into their initial ground state, and the electrons and electron holes recombine. However, before the electrons and electron holes recombine, a charge separation is produced between the negative electrons and the positive electron holes. These charged areas can react with other molecules on the photocatalyst's surface. In the case of the photocatalytic reduction of CO_2, the CO_2 and H_2O molecules react on the charged surface to produce organic compounds.

TiO_2 is the most commonly used photocatalyst, due in part to the fact that it is cheaply and easily commercially available. However, it takes high energy light (in the range of UV radiation) to excite its electrons. Since solar radiation is primarily lower-energy visible light and only 3% UV radiation, in terms of solar energy input the efficiency of this reaction is low. However, "doping" TiO_2 (meaning to introduce impurities such as carbon into its crystal structure) has been shown to reduce the light intensity needed to excite its electrons from the UV to the visible light region. Copper (Cu) is also often used as a co-catalyst with TiO_2. It is believed that the excited electrons from the TiO_2 rapidly transfer to the Cu particles before recombining with the electron holes. Thus, Cu would promote the reaction by separating the charged sites on the photocatalyst and increasing the amount of time available for molecular interaction at these sites.

In this paper, the efficiency of CO_2 reduction by the following photocatalysts is reported: commercial TiO_2, commercial TiO_2-Cu, C-doped TiO_2, C-doped TiO_2-Cu, undoped TiO_2, and undoped TiO_2-Cu. A Xenon lamp was used to irradiate the samples due to the similarity of its spectrum to that of natural sunlight. Results suggest that among the photocatalysts studied here, commercial TiO_2 is the most effective in producing total organic carbon (TOC). However, high-purity commercial TiO_2 is synthesized via a high-temperature (and thus high-energy impact) process. Among the samples synthesized via a low-energy process from low-purity titanium sulfate ($TiOSO_4$), C-doped TiO_2 was found to be more effective than undoped TiO_2. The addition of Cu had an inconclusive effect on the production of TOC. From these results it can be concluded that C-doped TiO_2 can be synthesized from an environmentally-friendly process to produce an effective photocatalyst for reducing CO_2 in aqueous solution to organic compounds.

Recommendations

Significant funding should be directed towards future research of this technology. Additional experiments should be conducted to improve the quality of C-doped TiO_2 synthesized from the low-energy process, such as by starting from higher-quality $TiOSO_4$ or by finding the optimal ratio of C to Ti. Implementation of this carbon sequestration technique should lead to a cheap, effective, efficient, and environmentally-friendly way to store CO_2 in organic compounds, thus reducing greenhouse gas emissions in the atmosphere without using additional fossil fuel resources.

A.2. 二氧化碳捕集与封存文献回顾

2006 年全球的化石燃料燃烧产生大约 290 亿公吨的二氧化碳，是大气中二氧化碳的主要来源。 近年来二氧化碳的排放量一直处于持续增长状态。 二氧化碳是一种温室气体，会造成气候变暖。 气候变化将带来一系列严重的后果，会增加与热相关的死亡和传染性疾病的传播，会增加旱灾、火灾和洪水的风险，还会增加暴雨的强度。 冰川融化将导致海平面上升。 由于温度的变化，原有的植被将减少，野生动物将被迫迁移寻找合适的栖息地。 而这些环境问题会加剧很多社会问题，比如饥饿、缺水，造成人们流离失所、政治不稳定和经济损失。 所以，气候变暖既危害自然生态系统的平衡，更威胁人类的食物供应和生存环境。 此外，还有能源安全问题，过度地依赖外来能源会大大增加能源消耗的成本和风险性。 比如政治分歧可能会导致燃料供应的限制--美国的电气网格线和石油/天然气管道由于途经多国而缺乏保障，能源运输网络很容易受到攻击。 基于上述原因，目前研究者们着力于研究两个方面：提高能源效率和开发能源的多样化，以极大可能地减少或解决化石燃料燃烧造成的能源环境问题，比如减排技术和可再生能源技术。

其中，二氧化碳捕集与封存（简称 CCS）技术对美国而言是一类很重要的化学工程研究课题。 CCS 技术包括温室气体减排和可再生能源生产。 当我读本科时，我有机会参加了几个 CCS 的研究项目。 今年夏天我在德国的鲁尔大学化学工程实验室做研究。 他们研究能吸收烟气中的二氧化碳的溶液，最常用的二氧化碳吸收剂是乙醇胺（简称 MEA）。 当溶液的温度升高时，或当压力降低时，二氧化碳的溶解度将下降。 当二氧化碳从溶液中释放出来时，它可以比较容易地被收集和储存。 而且溶液可以重复使用，吸收更多的二氧化碳。 此外，从去年开始我在密西西比大学的化学工程系和化学系研究了二氧化碳光催化反应的催化剂，进行了相关实验。 光催化表示一个需要光来反应的反应机理。 除了光以外，二氧化碳的光催化反应也需要一种催化剂来促进反应。 在有光和催化剂存在的条件下，二氧化碳与水反应，产生各种碳氢化合物。 因为二氧化钛是这种反应最常用的催化剂，我希望能通过掺杂来改进二氧化钛的光催化性能。 掺杂的意思是在二氧化钛的晶格结构中加入少量的其他物质。 在密西西比大学，我们研究了碳离子掺杂的二氧化钛。 我们认为二氧化碳的光催化反应很重要，因为它不仅能够减少二氧化碳的排放，而且能把太阳能转化成化学能储存于碳氢化合物中。 由于我对二氧化碳吸收剂和二氧化碳光催化剂的研究都很感兴趣，这个学期我查阅了相关的科研文献，了解了这两种技术的研究现况，希望对我和其他人在这领域的进一步研究有所帮助。

我会先讨论二氧化碳吸收剂技术的现况和问题。 研究者希望使用化学吸收剂来减少二氧化碳的排放。 常用的化学吸收剂类包括氨水类，碳酸钾溶液类和有机烷醇胺类。 我已经提到的 MEA 属于第三类，而且是最常用的，因为它的反应速度

快、价格便宜。 但是 MEA 的再生较困难，我读过的一篇科研文献分析了添加剂（比如 PZ，AMP）对 MEA 再生的影响。

文中的实验是测试加入添加剂后，MEA 溶液对二氧化碳的吸收速度和再生程度。第一类实验的结果是，PZ 的加入量越大，溶液对二氧化碳的吸收速度越快，而且吸收负荷越大。 PZ 能提高 MEA 的这两个特性是因为 PZ 分子含有两个氮原子，而 MEA 只含有一个氮原子。 因此，PZ 的吸收能力更强。 另一个结果是，PZ 的加入量越大，MEA 的再生程度越大。 这是因为 PZ 与二氧化碳的反应不如 MEA 与二氧化碳的反应那么稳定。 所以研究者认为 PZ 的最佳加入量是 8%。 采用 AMP 的结果差不多一样：AMP 的加入量越大，溶液对二氧化碳的吸收速度越快，吸收负荷越大，而且 MEA 的再生程度也越大。 AMP 能提高 MEA 的这三个特性是因为 AMP 是一种空间位阻胺，可以从不同的位置与二氧化碳反应，但生成的碳酸盐性质不稳定。 因为 AMP 的价格比 PZ 的高得多，所以研究者认为 4% 是 AMP 的最佳加入量。 最后，PZ 和 AMP 都能提高溶液吸收二氧化碳和再生的能力，可是添加 AMP 的效果比添加 PZ 的效果稍好。

MEA 是一乙醇胺，也常用的有机烷醇胺类的吸收剂包括二乙醇胺、三乙醇胺和 N-甲基二乙醇胺。 我读过的另一篇文献讨论了这三种吸收剂的种类和浓度对二氧化碳的吸收速度和效率的影响，而且讨论了吸收剂的再生情况的影响。

这篇文章中第一个结论是DEA和TEA 的吸收速度比MDEA 的快。 此外，DEA和TEA的浓度越大，它们的吸收速度越快。 相同浓度条件下，DEA和TEA的二氧化碳吸

收容量比MDEA的大，而且吸收剂的浓度越大，二氧化碳吸收容量的差距越大。 DEA的二氧化碳吸收容量比TEA的稍好一些。 而且，TEA的再生效率比DEA的大得多。

DEA和TEA的二氧化碳吸收效果好于MDEA。 因为MDEA跟二氧化碳的反应属于物理反应，而DEA和TEA跟二氧化碳的反应属于化学反应。 此外，DEA和TEA的反应速度跟它们的氮含量有关。 总之，我觉得作为吸收剂，TEA比DEA好；尽管DEA的二氧化碳吸收容量和速度比TEA的稍好，但我认为它们之间的差别并不明显。 可是，TEA的再生效率比DEA的好得多，因此我觉得TEA的好处比DEA的明显。 因为MDEA跟二氧化碳的反应是物理反应，我觉得MDEA对二氧化碳的吸收没有显著的效果。

基于这两篇文献的结论，如果有机会继续我在德国做的 MEA 研究，我希望通过添加 AMP 来提高 MEA 吸收二氧化碳的能力和再生能力。 我也想做进一步的阅读 -- 因为作为吸收剂的三乙醇胺（或 TEA）比二乙醇胺（或 DEA）好，我想知道如果 TEA 也比 MEA（或一乙醇胺）好的话，我应该考虑采用 TEA 替代 MEA。

我的第二个研究题目是二氧化碳的光催化剂--二氧化钛。 它的优点是具有良好的禁带宽度和比较强的氧化能力。 二氧化钛也很稳定，无毒，简单操作，而且反应只需要温和的条件，因此算是一种绿色治污新技术。 不过，二氧化钛反应需要紫外光来激发，而太阳的辐射多半是可见光，大大限制了二氧化钛的应用范围。科学家研究各种办法来改进二氧化钛的光催化性能。 其中，离子掺杂是一种有效途径。 我已经提到，在密西西比大学我们使用碳离子掺杂。 我阅读的文献中介绍了各种掺杂方法，比如金属离子掺杂、非金属元素掺杂和不同元素共掺杂。

在二氧化钛中掺杂金属离子有很多优点。 比如，金属离子能降低电子-空穴对的复合率，而且使二氧化钛的吸收波长范围扩展到可见光区域。 虽然金属离子能提高二氧化钛的活性，但金属离子的掺杂量存在一最佳值，过量的金属离子反而会降低二氧化钛的光催化活性。

非金属元素可以通过进入二氧化钛晶格或者取代氧空位进行掺杂。 非金属离子使二氧化钛禁带变得更窄，有助于二氧化钛利用可见光。 主要的非金属元素包括碳，氮，氟，硫等。 尽管有科学家成功地用碳来提高二氧化钛的光催化活性，但他们认为跟二氧化钛掺杂的最理想非金属元素是氮。

研究者也通过掺杂不同元素来研究不同的混合对二氧化钛有何影响。 研究表明，有的双金属共掺杂的二氧化钛比单一金属掺杂的有效。 不过，有的双金属混合不如单一金属那么有效。 而且，由于存在最佳的双金属混合比例，使得制备过程较为复杂。 科学家发现，双非金属和非金属与金属共掺杂都能提高二氧化钛的光催化反应性能。

另一篇文章分析了几种无机阴离子掺杂对二氧化钛的光催化性能的影响，因为阴离子具有比较高的氧化能力。 测试的阴离子包括钼酸根离子(MoO_4^{2-})、高锰酸根离子(MnO_4^{2-})、钨酸根离子(WO_4^{2-})和锡酸根离子（SnO_3^{2-}）。

研究者先分析不同阴离子与其掺杂量对二氧化钛薄膜光催化活性的影响。 他们发现阴离子掺杂量存在最佳值。 在这四种阴离子掺杂中，只有 SnO_3^{2-} 的掺杂能够提高二氧化钛的光催化性能，MnO_4^{2-}、MoO_4^{2-} 、WO_4^{2-}的掺杂都抑制了二氧化钛的光催化反应。 研究者在文中解释了这种现象：因为 MnO_4^{2-}、MoO_4^{2-} 和 WO_4^{2-}的

离子体积较大，所以即使在最佳掺杂量的情况下也会抑制二氧化钛的光催化性能。而 SnO_3^{2-}可以通过热处理产生 SnO_2，抑制了二氧化钛晶粒的生长，在最佳掺杂量的条件下能够提高二氧化钛的光催化活性。

基于这两篇文献的结论，因为研究者认为跟二氧化钛掺杂的最理想非金属元素是氮，我认为我将来的研究可以从碳离子掺杂转为采用氮离子掺杂。 不过，无论碳还是氮，好象都比无机阴离子掺杂有效得多。 此外，在这些掺杂方法中，非金属与金属共掺杂对提高二氧化钛的光催化性能是最有效的。 因为碳和氮是非金属元素，我想测试它们与一种金属离子共掺杂对二氧化钛的光催化性能会有什么影响。 我希望这种变化会改进我的研究，未来能大幅度地减少二氧化碳排放。