

**PHOTOELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE INTO
OXY-HYDROCARBON AND OXIDATION OF AZO DYE
SIMULTANEOUSLY**

by

Yun-Ta Yeh

A thesis submitted to the Faculty of the University of Delaware in partial
fulfillment of the requirements for the degree of Master of Civil Engineering

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ABSTRACT

Climate change is caused by greenhouse gases. The increased carbon dioxide (CO₂) in the atmosphere is considered the major factor of the climate change. Therefore, it is important to decrease the accumulation the atmospheric carbon dioxide. In this study, in order to save energy and prevent consume “energy” for producing “energy”, the reduction of carbon dioxide was applied in a photoelectrochemical (PEC) system using solar cell and N-doped TiO₂ thin film. In both systems, formic acid, formaldehyde, methanol, and methane were produced by the photoelectrochemical reduction of CO₂ while hydrogen was form by the water electrolysis. The yields of the products in the 0.1 M KHCO₃ aqueous solution were 1.55, 0.62, 2.02, and 2.16 μM for HCOOH, HCOH, CH₃OH, and CH₄, respectively, for the solar cell system and 2.29, 0.68, 1.91, and 3.94 μM, respectively, for N-doped TiO₂ thin film system. In order to save applied energy on hydrogen evolution instead of being used for CO₂ reduction, different concentration of methanol-based electrolytes were applied. Methanol electrolytes not only suppressed hydrogen formation, but also increased the yields of the products from photoelectrochemical reduction of CO₂. In addition, a differential first-order kinetic model was successfully applied to simulate the photoelectrochemical reduction of CO₂ on a copper electrode in KHCO₃ aqueous solution at ambient temperature and pressure in both systems. The reaction rate constant for HCOOH, HCOH, CH₃OH, and CH₄ were 1.30×10^{-8} , 4.26×10^{-6} , 1.68×10^{-5} , and $4.43 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$, respectively, for the solar cell system and

9.55×10^{-9} , 4.53×10^{-6} , 1.13×10^{-5} and $2.52 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$, respectively, for the N-doped TiO_2 thin film system. Furthermore, the degradation of an azo dye, namely, methyl orange (MO) in photocatalytic, electrochemical, and photoelectrochemical processes, was investigated in this study. The degradation of MO was operated simultaneously with the degradation rate of 9.33×10^{-5} , 8.31×10^{-5} , and $7.13 \times 10^{-5} \text{ s}^{-1}/\text{cm}^2$ for 0% methanol-based, 20% methanol-based, and 40% methanol-based, respectively, for the solar cell system. In addition, the study also investigated the kinetic rate constant of methyl orange via photoelectrochemical, electrochemical and photocatalytic processes using N-doped TiO_2 thin film system with the rate constant of 4.32×10^{-6} , 4.32×10^{-7} , and $1.50 \times 10^{-7} \text{ s}^{-1}/\text{cm}^2$, respectively, for N-doped TiO_2 thin film system.

Chapter 1

INTRODUCTION

1.1. Introduction

1.1.1. Problem Statement

As countries try to develop and grow their economies, their demand for oil increases, as the total available amounts of oil decreases. Although the amount of carbon dioxide is not the most of the emitted gas after inflammation, the emission of carbon dioxide is much higher than other greenhouse gases. According to the National Oceanic and Atmospheric Administration's (NOAA) report in 2011, the carbon dioxide concentration in the atmosphere reached 394.16 ppm. Compare to the report of the Intergovernmental Panel on Climate Change (IPCC) in 2000, it increases 24.16 ppm from 370 ppm. If human are not urged to take measures to reduce carbon dioxide levels, the high concentration of carbon dioxide will cause the global warming. As reported by the U.S. EPA in 2007, the environmental crisis caused by global warming seriously influences human, such as polar ice cap melting and sea level rise to threaten low-lying countries. In addition, droughts, inundation, conflagration, and storms cause human casualty and animal extinction.

Due to the global warming issue which has been concerned recently, in order to decrease the impact caused by global warming, carbon dioxide, which is regarded as one of the key greenhouse gases, Kyoto Protocol have been developed in 1997. The Kyoto mechanism includes emissions trading, the clean development

mechanism, and joint implementation. Also, capture technologies have been developed for decades, including electrochemical reduction, photochemical reduction, hydrogenation of carbon dioxide in aqueous solution, biochemical procedures, and thermochemical procedures.

In the development of reducing carbon dioxide to fuels, electrochemical approach has been one of the most popular reduction reactions for the last decades. Compared to storing electricity in batteries or as hydrogen, carbon based fuels are more easily to be used within the existing infrastructures, producing a much higher energy density. And the converting electrical energy to chemical energy process was involved in order to produce this carbon based fuel, thus highlighting the importance of electrochemistry [1]. Based on the general carbon-based energy cycle concepts, water, methanol and methane would be produced by reacting carbon with electrolytic hydrogen. Mikkelsen *et al.* (2009) [2] reviewed that chemical reaction, electrochemical reduction reaction and photocatalytic reduction have been done by many researchers [1, 3-10]. Chemical reduction of carbon dioxide is thermodynamically feasible in the presence of strong reducing agents such as metallic elements (Ti, Fe) and borohydride (BH_4^-). However, it requires the addition of electron-donating chemicals for chemical reduction of carbon dioxide. Photocatalytic, such as TiO_2 , reduction is another way to reduce carbon dioxide. Dey (2007) reviewed chemical reduction of CO_2 using TiO_2 photocatalysts [11]. There are two pathways to yield the hydrocarbons, $\text{CO}_2 \rightarrow \text{HCOOH} \rightarrow \text{HCOH} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4$ [7, 12, 13] and $\text{CO}_2 \rightarrow \text{CO} \rightarrow \text{C} \cdot \rightarrow \text{CH}_2 \rightarrow \text{CH}_4$ [14-17]. The former mechanism has been anticipated on the basis of the results obtained in condensed media, while the latter has

been proposed based on the finding in photocatalytic reduction of high pressure CO₂ using TiO₂ photocatalysts in suspension.

An alternative to photocatalytic reduction of carbon dioxide is electrochemical reduction. Spataru *et al.* (2003) studied reduction of carbon dioxide at RuO₂-coated diamond electrodes and suggested the formation of formic acid and methanol [18]. Aydin and Koleli (2004) reported that, under high pressure in methanol, the conversion of carbon dioxide on a polypyrrole electrode can electrochemically produce HCOH, HCOOH, and CH₃OH [19]. Kaneco *et al.* (2006) investigated the electrochemical reduction of carbon dioxide in methanol solution at high pH over copper electrode and reported the production of ethylene [20]. It has been illustrated that the electrode materials and electrolyte used affect the yield of CO₂ reduction products. Some researchers reported that only copper was able to generate a significant amount of hydrocarbon such as methane and ethylene among a total of 16 electrodes studied [10].

However, such process may consume much electricity in order to produce high quality of methane and methanol, leading to consuming “energy” for producing “energy” and non-environmental friendly. A key improvement along the road to solve this tricky problem is photoelectrochemical reaction (PEC). Sun *et al.* (2010) reported that PEC is a perspective technology on water splitting [21]. Zhou *et al.* (2009) successfully applied PEC system to generate hydrogen over carbon-doped TiO₂ photoanode [22]. Although this reduction reaction of carbon dioxide was not popularly used and not fully developed due to the fact that electrons are generated by the photo cells (i.e., photo cells might refer to solar cells or TiO₂ cells, depending on the

materials), researchers should still put emphasis on the PEC approach and keep developing and investigating it for further application.

1.1.2. Hypothesis and Objectives

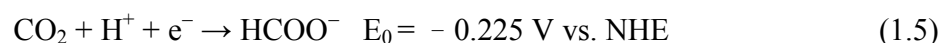
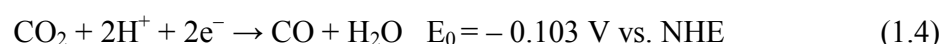
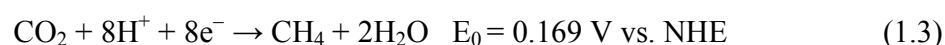
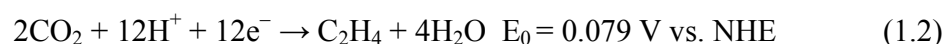
In this study, a commercial solar cell and a N-doped TiO₂ thin film were applied in a photoelectrochemical process. This technology is based on solar light as the solar energy source and required no chemicals in the process. In our hypothesis, the carbon dioxide can be converted into energy-containing organic carbons such as methane, alcohols and benign organic acids that can be reclaimed using photoelectrochemical approach. In addition, the azo dye can be oxidized simultaneously. For solar cell approach, all electrons are converted from the photons. The converted electrons can be used as reducing agents for carbon dioxide reduction and the anode of the commercial solar cell is able to be used for oxidation reaction for organic compounds, namely, methylene orange. For N-doped TiO₂ thin film approach, the electrons converted from photons can be used as reducing agent in the cathode and the holes can be used for degradation of azo dye in the anode.

This study deals mainly to study a sustainable technology for recycling carbon dioxide as energy-containing organic compounds such as alkanes, alcohols, and organic acids and degradation of selected azo dye (methyl orange). The research has the following three specific objectives: (1) to investigate the effect of CO₂ solubility for the photoelectrochemical reduction of carbon dioxide in aqueous solution, (2) to study the kinetic mechanism for the photoelectrochemical reduction of carbon dioxide at copper electrode via solar cell system and N-doped TiO₂ thin film system, and (3) to study the degradation of selected azo dye (methyl orange) via photoelectrochemical process.

1.2. Literature Review

1.2.1. Background

For photoelectrochemical reduction of CO₂, the electrode (cathode) material plays very significant roles. And the electrode substrates could determine strongly the yield and type of the reduced chemicals [10]. Based on the previous researches, the electrode substrate metals may be categorized in accordance with product selectivity [6]: (1) Cu; (2) Au, Ag, Zn, Pd and Ga; (3) Pb, Hg, In, Sn, Cd and Tl; (4) Ni, Fe, Pt and Ti. Table 1.1 shows the Faradaic efficiencies for the major products [6, 23]. As shown in Table 1.1, among all the metals, copper is proved to be a unique material of electrode for CO₂ reduction with its significant current densities if the major reduced products are hydrocarbons and alcohols [4-6, 24, 25]. During the reduction of CO₂, the primary reactions on the copper electrode surface are shown below (with the standard potentials calculated by formation energies):



As can be seen from the reactions (1.1) to (1.5), pH value of the reaction environment plays an important role on whether these reactions would occur or not. Figure 1.1 represents the equilibrium potentials as a function of pH for the principal overall CO₂ reduction reactions (at 25 °C) (the reactions are typically performed over the range of the pH values), and from Figure 1.1, we can easily understand the relationship between the potentials and pH values of the solution, leading to more

precise reduction product selectivity [26]. Based on the thermo-dynamical point of view, methane and ethylene would be produced at a less cathodic potential than hydrogen; whereas, it does not occur kinetically [26].

Table 1.1. Faradaic efficiencies (%) for various reduced products from the electrochemical reduction of CO₂ using several metal electrodes [6].

Electrode	CH ₄	C ₂ H ₄	C ₂ H ₅ OH	C ₃ H ₇ OH	CO	HCOO ⁻	H ₂	Total
Cu	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Au	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	0.0	0.0	0.0	0.0	0.0	0.0	99.7	99.7

Some researchers have suggested that the CO₂ reduction product distribution is highly influenced by the applied potential [27-29]. When it comes to CH₄, Frese *et al.* (1988) demonstrated that the onset potential was around -1.5 to -1.6 V vs. SCE (at pH 7.6 and 22 °C) and the maximum efficiency, i.e., 50% current efficiency was occurred around -1.95 V. The potential between these two levels (-1.5 and -1.95 V), i.e., around -1.7 V, the CO production would exceed CH₄ production. The electrode preparation and the amount of mass transport affected the exact point of

the change of the dominant product from CO to CH₄, especially for higher stirring leading to more CO. One explanation for this phenomenon was that CO would be removed effectively at higher mass transfer before further reduced to CH₄. Some researchers believed that CO was an intermediate product during the reduction of CO₂ to CH₄ [27-29]. According to this hypothesis, Ito *et al.* (1989) measured a larger set of products, with different products under various potentials [27]. The initial product was formate at -1.35 V vs. Ag/AgCl/saturated KCl (at around 30% current efficiency); CO was formed at -1.47 V, ethylene was formed below -1.54 V, and then CH₄ below -1.65 V. When the potential exceeds -1.75 V, the hydrogen would become the dominate specie, resulting in CH₄ production decay. Hori *et al.* (1989) also reported the same data tendency. Moreover, Hori *et al.* (1989) suggested that partial currents would be calculated for different products, as shown in figure 1.1 along with the estimates of the local pH and CO₂ concentrations at the electrode surface [28-30]. At the beginning of the reaction, CO and formate were first generated, and when the potential up to -1.12 V, the hydrocarbon compounds start to form: ethylene was generated first, and then methane. These series reaction would speed up, becoming the dominating reduction compound over formate and CO when the potential was up to -1.35 V. In addition to formate, methane and CO, other products, such as ethanol, acetic acid [31], propanal, 2-propen-1-ol, propanol, were suggested from CO₂ reduction at the copper electrode.

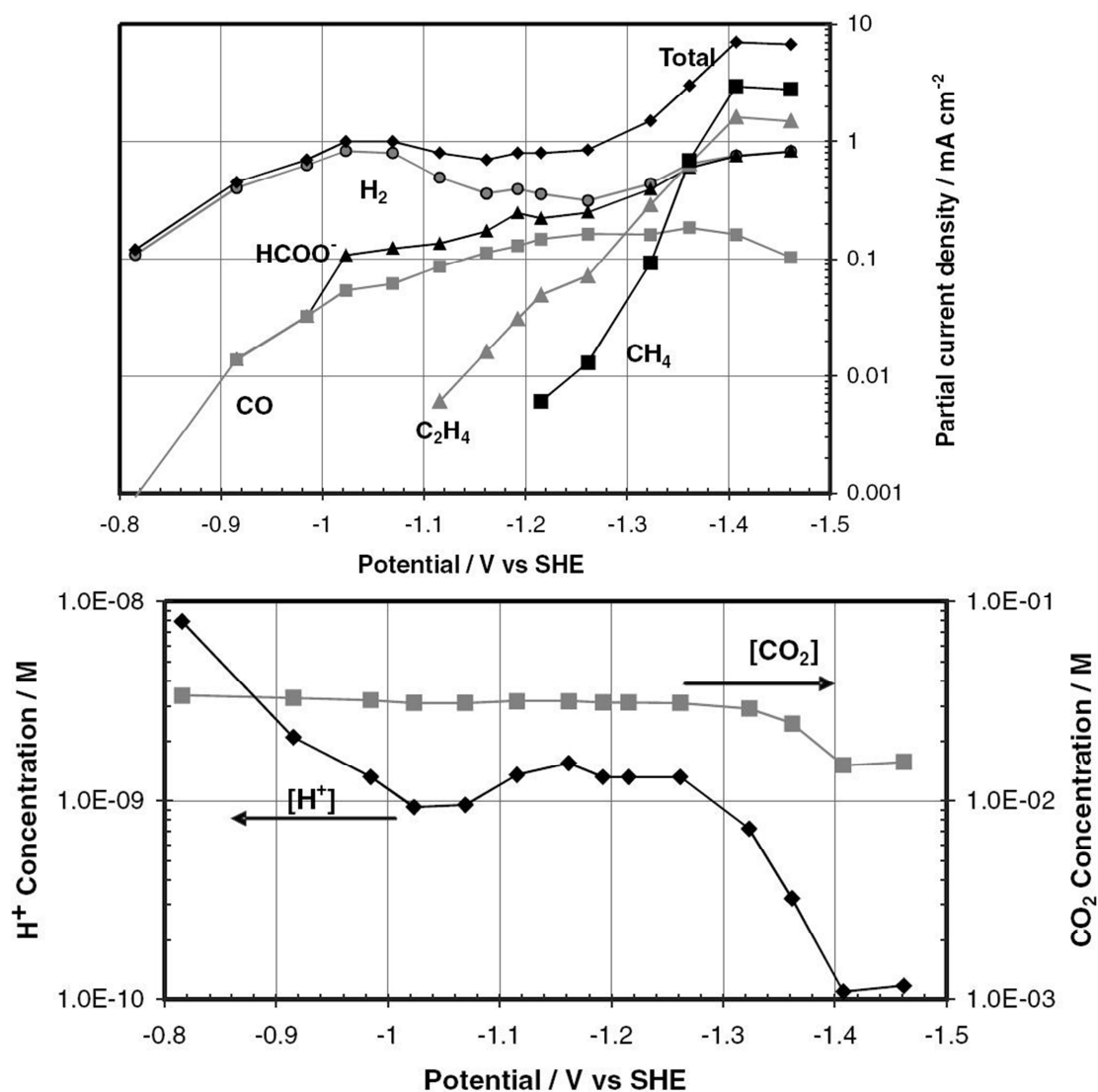


Figure 1.1. Partial current data from Hori *et al.* [24] (0.1 M KHCO₃, 19 °C, CO₂ bubbled, bulk [H⁺] = 1.55 × 10⁻⁷, bulk [CO₂] = 3.41 × 10⁻² M. (Estimated local [H⁺] and [CO₂] values for polarization measurements from [30])

1.2.2. The CO₂ Reaction Step

The CO₂ reduction reaction began with the reaction of CO₂ to form CO. Interestingly, this reaction would not always occur directly; instead, it sometimes would compete with the formation of formate. As seen in figure 1.1., at less negative potentials, hydrogen, formate and CO are the three dominant reactions. However, during the reaction, CO would be formed and adsorbed on the electrode surface (copper) and then proceed further reaction to hydrocarbon, resulting in being hard to understand the whole picture of the CO₂ reduction reaction. Therefore, in order to understand the reaction step of CO₂ reduction at the copper electrode, it's necessary to study the same reaction occurred at the similar metals to copper, such as silver and gold, due to the fact that CO would be easily desorbed from the electrode surface and would not further react to any significant extent [26].

Take gold as an example. The reaction at gold electrode was first order in CO₂ with a Tafel slope of around 120 mV decade⁻¹, thus leading to the fact that the rate determining step is thought to be the initial CO₂ reduction [32, 33]:



On the other hand, for single crystal silver electrodes, the results shows that the CO₂ to CO reaction would occur more likely on Ag (110), as can be seen from figure 1.2. [30]. Using Ag (110) may enhance the formation of formate; however, the reaction will slow down below the potential -1.5 V vs. NHE. The reason for this situation may be due to the consumption of the CO₂ concentration near the electrode surface by the CO formation reaction [34].

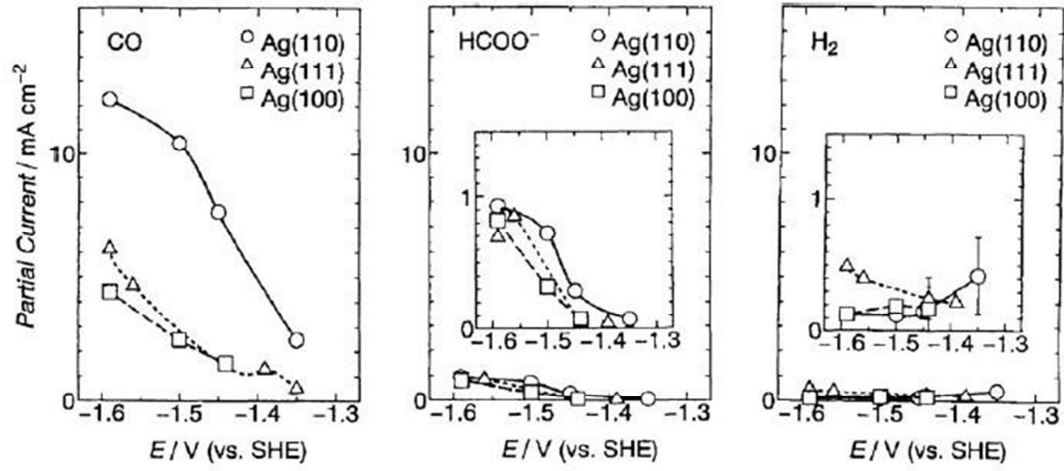


Figure 1.2. Partial current densities on silver single crystals (0.1 M KHCO₃, CO₂ saturated, from Hori *et al.* [34])

The following two reactions can explain the formate formation, by protonation then reduction:



As mentioned before, the CO₂ molecule would become CO₂^{·-}, which is adsorbed on the electrode surface, and then with the coordination of oxygen and a proton adding at the carbon, the reaction (7) can occur. The reaction, reduction of CO₂ to formate, was demonstrated to have a Tafel slope characteristic of a second electron transfer r.d.s. at low overpotential, and it would shift to the first electron transfer r.d.s. at medium to high overpotential, when using high hydrogen overpotential electrodes [35]. That is to say, at low overpotential, reaction equation (8) occurs; whereas at medium to high overpotential, reaction equation (6) would take place. A brief summary for these reaction pathways were shown in figure 1.3. In this schematic

overview, there are two main pathways: one leading to formate formation, and the other to CO and hydrocarbon formation. In these reactions, CO molecular which adsorbed on the electrode surface was regarded as the primary cause of surface inhibition. On the other hand, as shown in this scheme, hydrogen adsorption would occur within the reaction when the reaction involves hydrogenation, and the corresponding mechanism involved in this hydrogenation process can be known by understanding the hydrogen evolution on copper.

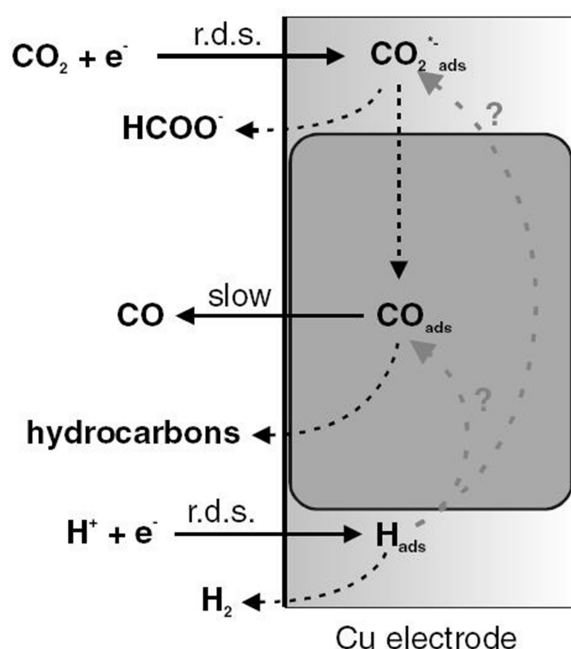


Figure 1.3. The main reaction pathways at the electrode surface, with adsorbed CO blocking the majority of the surface and hydrocarbon products being formed by the further reduction of adsorbed CO [35].

Another way to understand the mechanism for CO₂ reduction at copper is steady state polarization. But in order to get the steady state polarization data, the

electrode surface must not change, and no trace impurities in the electrolyte which might deposit on the electrode surface [36]. Figure 1.4., which was the results of some previous studies, shows the current efficiencies at different potentials, [29, 32]. As can be seen from Figure 1.4., both data present that initially, formate and CO appear, and formate is the dominate specie at the beginning. When concentration of CO increases, hydrogen evolution was suppressed. The next step would be CO transformation to hydrocarbons, occurring at around -1.2 V, with first ethylene then methane appearing. Moreover, at such potential, the total current for the pathway, which was provided by figure 1.4, causes that the dominate specie becomes CO plus its products, instead of formate formation. When the potential increases up to -1.4 V, the steady state CO coverage drops and the CO_2 concentration around the electrode surface decreases (see Figure 1.1), hydrogen evolution starts to recover. This suggested that the two references [29, 32] showed the similar trends.

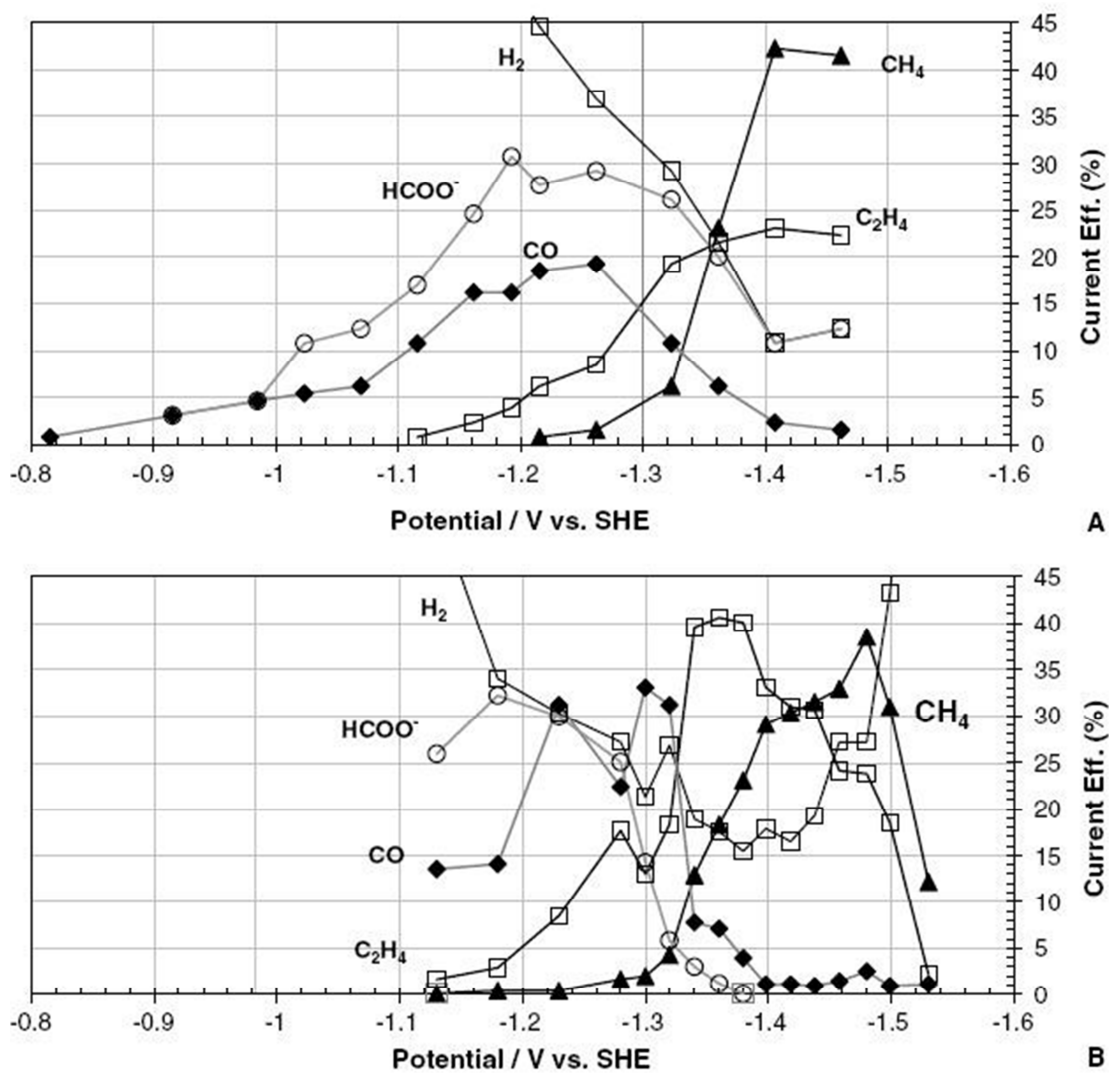


Figure 1.4. Current efficiencies at different potentials (0.1 M KHCO₃, CO₂ bubbled). A: data from [29], B: data from [32] (25 °C)

1.2.3. Factors Affecting CO₂ Reduction Reaction

Poisoning species on electrode and the electrolyte types

In order to enhance the accuracy and reproducibility, Hori *et al.* (1986) suggested that the electrodes must be carefully prepared before the experiments. This preparation, typically, refers to mechanical polishing followed by electropolishing in 85% phosphoric acid, and the detailed preparation procedure was published elsewhere [37]. And the electropolishing can also remove the stressed surface layer (produced by polishing) and the impurities on the electrode surface [38]. In addition to good preparation of electrode, there is one other important factor which should be noticed - poisoning species on the electrode surface. This poisoning cover would cause all the Faradaic efficiencies suddenly decreasing seriously after several tens of minutes from the beginning of the reduction reaction [39-42]. The electrode would fail in the original high catalytic activity [39-42]. Yano *et al.* (2008) reported that using pulse electrolysis could not only control and inhibit the poisoning species depositing on the copper electrode but enhance the C₂H₄ formation selectivity by varying the electrolytic conditions [10]. Furthermore, some researchers suggested that the electrolyte should be prepared carefully [28, 36]. If the electrolyte contains some impurities, the electrode might be covered with these impurities, leading to electrode characteristics change and losing the catalytic activity for CO₂ reduction.

Temperature and pressure

According to the research by Hori *et al.* (1986), the reaction temperature would affect the reduction product distribution [4]. Lower temperature (near 0 °C) might cause little change in the current efficiency for formate formation, and lead to decreasing efficiencies for hydrogen evolution and ethylene formation and increasing efficiency for methane formation [4]. Kaneco *et al.* (2002) also reported the same

tendency, with potentiostatically at -2.0 V vs. Ag/AgCl/saturated KCl in 0.65 M KHCO_3 over the range from 15 to -2 °C [43]. Some researchers also found that there was a shift in the obvious Tafel slope for the methane partial current from 93 mV decade⁻¹ at 22 °C to 520 mV decade⁻¹ at 0 °C. Moreover, lower temperatures could also affect adsorption equilibria and enhance CO_2 solubility.

Increasing CO_2 working pressure not only could enhance CO_2 solubility but also the reduction product distribution [44]. Hara *et al.* (1994) reported that increasing CO_2 working pressure from 0 to 60 atm at a constant current of 163 mA/cm², the dominant specie was shifted from hydrogen to hydrocarbons, and the current efficiency could reach up to 44% by around 10 atm of CO_2 . If keep increasing the CO_2 working pressure up to 20 atm, the current efficiency for hydrocarbon formation would decrease to 12% but the efficiency for formate and CO formation would rise to around 30% .

1.2.4. Thin Film Electrodes and Surface Modification

Several researchers reported the surface modification for photoelectrochemical cell [45-48]. For example, Nakato *et al.* (1998) used the formation of silicon-halogen termination on one side of the n-type Si chip to modulate its surface band energies [49]. And because of the presence of band bending in the n-Si chip in a photostationary state, this surface asymmetry performs an efficient solar-to-chemical conversion, resulting in efficient electron-hole separation. Size-quantized CdS nanoparticles with 2-aminoethanethiol were modified and immobilized on an electrode with the use of glutaraldehyde as a crosslinking agent [50]. In the photoelectrochemical behavior of the electrode, the quantum size effects of the immobilized nanoparticles on the metal electrode were retained [48]. With the similar

concept, Shiga *et al.* (1998) developed a TiO₂ thin film electrode by way of coating a TiO₂ colloidal solution on a F-doped SnO₂-glass substrate [51]. This TiO₂ film electrode had the photoelectrochemical current-potential curves, which was similar to those for single crystal n-TiO₂ electrodes, after annealing treatment [43, 46].

1.3. Summary

The development of photoelectrochemical reduction of CO₂ was investigated and reviewed in this article. The reduction of CO₂ to formate and hydrocarbon species was a complex reaction involving multiple-step pathways and sophisticated mechanisms. Depending on different electrode surface structure, local conditions, such as pH, CO₂ concentration in the electrolyte, CO₂ pressure in the reaction cell, temperature, and so on. However, because of the difficulty in generating high current and potential, which are essential for hydrocarbon compounds formation, by photo cell, photoelectrochemical reduction of carbon dioxide isn't fully developed, meaning lots of efforts waiting us to do in order to accomplish the goal: using environmental-friendly nature energy (sun light) to generate useful "energy".

Chapter 2

PHOTOELECTROCHEMICAL REDUCTION OF CO₂ VIA N-DOPED TITANIUM DIOXIDE THIN FILM

2.1. Introduction

Carbon dioxide (CO₂) is one of the primary contributors to greenhouse effect and thus one of the major reasons of global warming. Recently, there are increasing attempts to consider it a resource and a feedstock rather than a waste with a cost of disposal [9, 52]. In general, chemical reduction of carbon dioxide is thermodynamically feasible in the presence of strong reducing agents such as metallic elements (Ti, Fe) and borohydride (BH⁴⁻) [53]. However, it requires the addition of electron-donating chemicals. Therefore, the modified chemical processes such as electrochemical (EC) [4, 29, 38, 54-57], photocatalytic (PC) [18, 58-63] and photoelectrochemical (PEC) [64-68] methods have been applied to reduce carbon dioxide. Electrochemical CO₂ reduction is achievable as the working electrode surface can result in lower overpotentials. The providing electrons can reduce carbon dioxide into formic acid, formaldehyde, methanol and methane. Nevertheless, as far as clean technology is concerned, electrochemical reduction, which still requires electricity, cannot be qualified as totally sustainable. An alternative to electrochemical reduction of carbon dioxide is photocatalytic reduction using a photocatalyst such as TiO₂. While photocatalytic conversion of carbon dioxide to methane and other energy-rich compounds is possible, there are problems. First, the photocatalytic efficiency was generally low at less than 10%. This is because holes that are generated at the same

time as electrons oxidize the reaction products or intermediates back to the parent compound, i.e., carbon dioxide. This has prompted several researchers to use hole scavengers such as 2-propanol, methanol and ethanol to increase the yield [69]. However, the use of organic hole scavengers is counterproductive. This led to researchers to design the photoelectrochemical process using visible light sensitivity materials to convert carbon dioxide to energy-rich organic compounds. The first use photocatalytics as a photoelectrode to photoelectrochemical reduce of CO₂ can date back over 30 years [67]. Inoue *et al.* [64] accordingly examined the photoelectrocatalytic reduction of CO₂ in aqueous suspensions of TiO₂, ZnO, CdS, GaP, SiC and WO₃ powders. Furthermore, various p-type semiconductors have been used, including p-InP, p-GaP, p-GaAs, p-SiC and p-CdTe for the application of CO₂ reduction [68, 70-74]. These novel materials can utilize solar energy, a renewable and green energy, to generate electrons to be the reductant for CO₂ reduction reactions. Among these materials, TiO₂ has been the most studied because of its attractive photocatalytic activity, chemical stability, nontoxicity, and low cost. However, the TiO₂ high band gap between 3.2 – 3.4 eV obstructs application. In other words, only UV light, which occupies less than 5% of the solar spectrum, excites TiO₂. Herein, this paper applied a nitrogen doped TiO₂ thin film (NTTF), prepared by pulsed laser deposition (PLD) method, to be the photoanode in the PEC system. The NTTF has a band gap of 2.0 eV and can be excited by the visible light. To the best of our knowledge, there is no report applied N-doped TiO₂ thin film as a photoanode to proceed the PEC CO₂ reduction.

Many researchers have studied various effective methods for photoelectrochemical CO₂ reduction. Only a few authors engaged in the development

of kinetic model for the formation of CO₂ reduction products. Lo *et al.* [75] and Tan *et al.* [61] applied Langmuir-Hinshelwood model to simulate the formation rate of CO₂ reduction products. Koci *et al.* [76] subsequently modified the model from Tan *et al.* [61] to predict the liquid and gaseous products. Dey [11] reviewed chemical reduction of CO₂ using TiO₂ photocatalysts. There are reaction pathways to yield the final product of CH₄, viz. CO₂ → HCOOH → HCHO → CH₃OH → CH₄ and CO₂ → CO → C· → CH₂ → CH₄. The former mechanism has been anticipated on the basis of the results obtained in condensed media, while the latter has been proposed based on the findings in photocatalytic reduction of high pressure CO₂ using TiO₂ photocatalysts in suspension. In this study, a differential solution method was employed to simulate the formation of CO₂ reduction products, i.e. HCOOH, HCOH, CH₃OH and CH₄, for the first time. It would be a helpful tool to analyze the photoelectrochemical CO₂ reduction processes and provide a better understanding for CO₂ reduction reactions as well.

2.2. Materials and Methods

2.2.1. Materials

The electrolyte solution was prepared by dissolving a proper amount of potassium bicarbonate in deionized water prepared in the laboratory using a water-purification system (Mega-Pure System, Model MP-290). Potassium bicarbonate, formaldehyde (purity>37%), methanol, acetonitrile, Sodium hydroxide, sulfuric acid were purchased from Fisher Scientific, USA. Sodium chloride (purity>99%), formic acid (purity>99%), and phosphoric acid (purity>85%) were purchased from ACROS, USA. 2,4-dinitrophenylhydrazine (DNPH), and methyl orange (purity>85%) was

purchased from Sigma-Aldrich, USA. A copper wire, curled to be a coil of 0.9 cm in diameter with length of 35 cm (11 inches) and 1 mm in width, was purchased from Fisher Scientific, USA.

2.2.2. N-doped TiO₂ Thin Film Preparation

Pure TiO₂ target was prepared from P25 Degussa particles (Sigma-Alrich, USA). The target was ablated under partial Nitrogen and Oxygen atmosphere on an ITO coated glass (SPI supplies Inc., PA, USA) by PLD technique. The description about the setup is given in Lin *et al.* [77] in detail. Briefly, a KrF excimer laser (Lambda physic LPX 305, $\lambda=248$ nm) was applied. Base pressure in the system was kept below 0.01 Pa with a turbo molecular pump and a mechanical pump. A mixture of N₂ and O₂ (4:1) was purged to the system, while the chamber pressure was maintained at 13.3 Pa. Two 500 W halogen lamps were used as irradiative heating source to control the substrate temperature up to 600 °C. Eventually, the target was ablated for 20 minutes.

2.2.3. Characterization of N-doped TiO₂ Thin Film

Microstructure and morphology of the synthesized materials were observed on a Scanning electron microscopy (SEM, JSM 7400F). The crystal structures of TiO₂ thin film (TTF) and NTTF were characterized by X-ray diffraction (Rigaku D-Max B) with Cu K α radiation ($\lambda = 1.54$ Å) operating at a voltage of 30 kV and a current of 30 mA. Samples were analyzed by Bragg Brentano geometry and are scanned with 0.02 step size between 20–80°. The crystal structures are solved by maud software using rietveld method. UV-Visible spectroscopy, collecting transmission and reflectance data by Perkin Elmer instruments (Lambda 750), was

applied to investigate the absorbance spectra of NTTF over a range of 300–800 nm. X-ray Photoelectron spectroscopy was collected with Omicron surface science instruments. High resolution XPS spectra of N 1s, Ti 2p and C 1s regions were collected with a step size of 0.02 and 0.2 second dwell time. The resulting spectra were fitted by XPSPEAK with Shirley background.

2.2.4. Photoelectrochemical Reduction of Carbon Dioxide and Degradation of Methyl Orange via N-doped TiO₂ Thin Film

All PEC experiments were carried out in a three-electrode system at room temperature. A saturated calomel electrode (SCE) was selected as the reference electrode. The NTTF was used as the working electrode (6.25 cm²) and a copper wire (Fisher Scientific, 155451A-16AWG-B16, od: 1 mm, length: 163 cm, total surface area: 51.2 cm²), pretreated by switched potential of 10 volts in 0.1 M H₂SO₄ (Fisher Scientific, USA), was used as the counter electrode. The electrolytes used for anodic chamber was 0.1 M NaCl (ACROS, USA) and for cathodic chamber was 0.1 M KHCO₃ (Fisher Scientific, USA). In the cathode chamber, carbon dioxide gas was bubbled into 0.1 M KHCO₃ (pH = 8.3) solution for 1.5 hours at a rate of 12 mL/s until saturated (pH = 6.8). A self-designed H-type reactor was made to separate the anode and cathode for better evaluation for the MO degradation. These two chambers were connected with a cation exchanged membrane to keep the ion balance in the system. A quartz window (7 cm²), on the side of the anode chamber, was used to provide good optical quality. The potential for both current-potential measurement and PEC degradation was controlled by a model AFRDE 4 potentialstat (Pine Instrument Inc., USA). Monochromatic excitation source (Model RF-5301, Shimadzu, Japan) was applied as the light source for photoactivities tests of NTTF. For PEC degradation, the

light source was 100 W Xe lamp with the average intensity of incident light was 3.12 mWcm^{-2} , measured by a high sensitivity thermal sensors (Model 3A-P-SH-V1, OPHIR, USA). The schematic diagram was shown in figure 2.1 (a) and figure (b). The gaseous and liquid samples of CO_2 reduction products were taken 5 times with the interval of 1 hour for each experiment. The instruments and experimental conditions for the photoelectrochemical reduction of CO_2 are listed in Table 2.1.

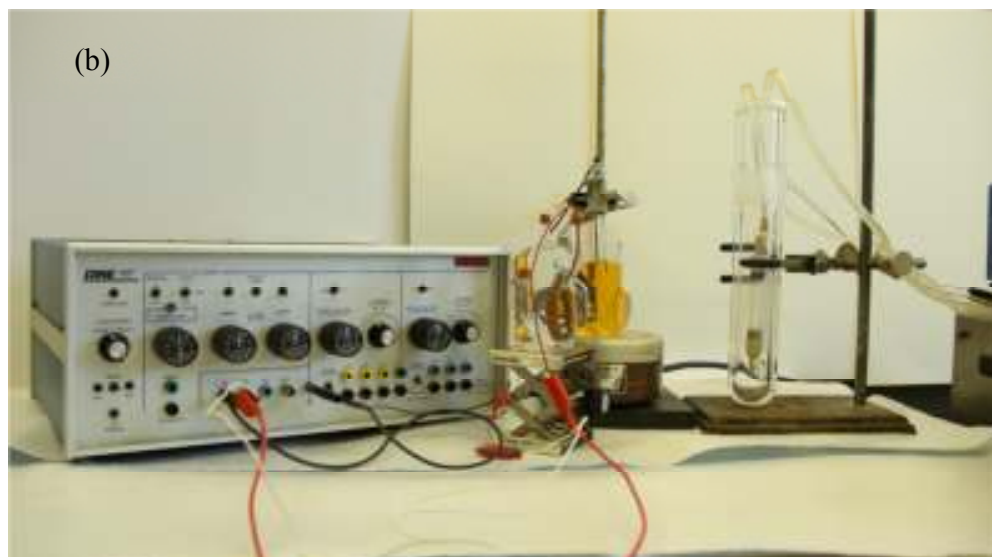
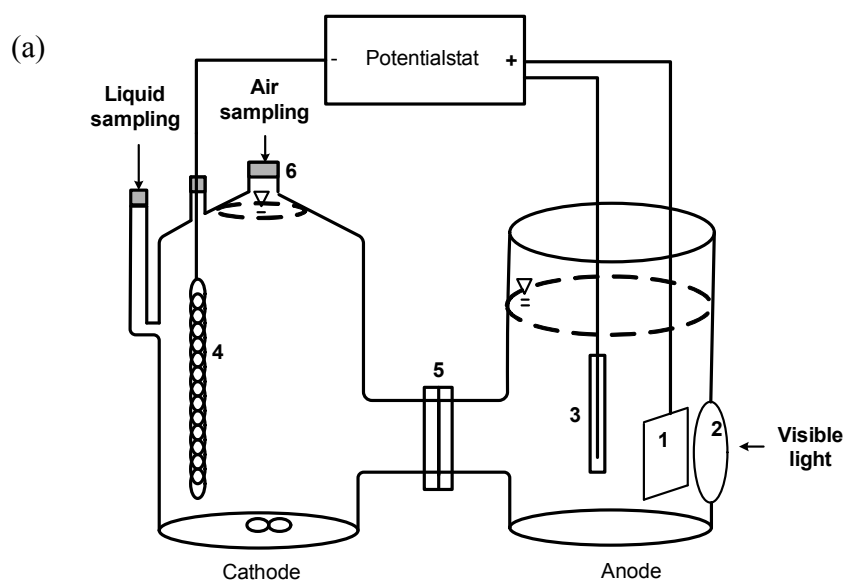


Figure 2.1. (a) Schematic diagram of photoelectrochemical system: (1) photoanode (N-doped TiO_2 thin film), (2) quartz window, (3) reference electrode (SCE), (4) counter electrode (copper wire), (5) cation exchange memberane and (6) septum. (b) photo of experimental setup.

Table 2.1. Apparatus and experimental condition of N-doped TiO₂ thin film system

Cell	H-type cell
Potentiostat	Model AFRDE 4, Pine Instrument Inc., USA
Monochromatic excitation source	Model RF-5301, Shimadzu, Japan
Working electrode	N-doped TiO ₂ thin film (N:O=80:20; area: 4 cm ²)
Counter electrode	Copper wire (Fisher Scientific, 155451A-16AWG-B16, od: 1 mm, length: 163 cm, total surface area: 51.2 cm ²)
Reference electrode	SCE (+0.24 volt vs. SHE)
Catholyte	0.1M KHCO ₃ in 0–50% methanol
Anolyte	0.1 M NaCl in 1ppm Methyl Orange
Carbon dioxide	99.9999% purity
Bias potential	2 volt vs. SCE
Temperature	Room temperature
Gas products analyzer	GC-FID/ GC-TCD (5890 series II, Agilent, USA)
Liquid products analyzer	HPLC with UV detector (1100 HPLC, Agilent, USA)
Irradiation source	100 W Xe lamp

2.2.5. Electrode Preparation

Before each experiment, copper wire was pretreated by reversed the polarity of 10 volts in 0.1 M H₂SO₄ every 15 s with a total time of 2 min. The cleaned copper wire electrode was rinsed with distilled water. The platinum electrode was dipped in 1 M H₂SO₄ and connected to 4.5 volt the power supply. A copper wire was

used as the counter electrode. The polarity was reversed every 15 s and the platinum electrode was continuously cleaned for 2 min. After cleaning the platinum electrode, it was rinsed with distilled water.

2.2.6. Analytical Methods

The gas products, hydrogen, was analyzed using a HP gas chromatography system (5890 Series II) with TCD detector (Packing: Alltech Hayesep D 100/120, Tubing: 1/8'' Nickel, Length: 20', carrier gas: Helium at 30 mL/min, oven temp.: 35 °C, injection and detector temp.: 120 °C, and sample volume: 100 µL).

Methanol and methane were analyzed using gas chromatography (5890 Series II) with FID detector (Packing: SUPELCO Supel-Q PLOT, fused silica capillary column, 30 m × 0.32 mm). The flow rate of carrier gas (Helium) and fuel gas (air, and hydrogen) were 3, 32, 300 mL/min, respectively. For methanol measurement, oven, injection, and detector temperature were set as 50, 100, and 250 °C, respectively. The injected volume was 2 µL. For methane measurement, oven, injection, and detector temperature were set as 50, 100, 250 °C, respectively. The injected volume was 1 mL.

The liquid sample, formic acid, was analyzed using a Dionex ion chromatograph system with a GP50 pump, ED 40 conductance detector and a AS 40 automated sample. NaOH was used as the mobile phase. The separation part was an IonPac AC20 column (4 × 250 mm). The flow rate of sodium hydroxide effluent was 1 mL/min with a concentration gradient to assure satisfying separation and detection limit. A 200 µL injection loop was used for formic analysis.

Before analyzing formaldehyde, the samples were derivatized using 2,4-dinitrophenylhydrazine (DNPH). The reagent solution was modified according to Lin [78] by dissolving 5 mg DNPH in 40 mL of solution containing concentrated HCl (12M), water, and acetonitrile in the ratio of 3.5:1:0.52 (v/v/v). The 1.5 mL sample was derivatized by adding 1.5 μ L derivatizing reagent in a 2 mL vial. The vial was capped and shaken for 20 seconds, and the reaction was allowed to proceed for 30 min at ambient temperature. Formaldehyde-DNPH was measured by High Performance Liquid Chromatography (HPLC) with a UV detector (hp, Hewlett Packard series 1100). The separation part was a Varian Inertsil 5 μ ODS-2 column (150 $\times$ 4.6 mm). The HPLC system was operated with binary gradients consisting of acetonitrile and acidified water with H₂SO₄ at pH 3.0. The flow rate was 1.0 mL/min. The column was at an ambient temperature. The injection volume was 60 μ L.

Methyl orange samples were measured using UV-Vis (HP 8452A diode array spectrophotometer) over the wavelength of 300 to 600 nm. The absorbance of MO was 450 nm.

2.3. Results and Discussion

2.3.1. Characterization of N-doped TiO₂ Thin Film

Figure 2.2 showed the XRD characterization results of the N-doped TiO₂ thin film and pure TiO₂ thin film. After sintered at 600 °C, both NTTF and TTF structures showed peaks at 25°, 38°, 54° and 63° corresponding to anatase phase. This crystal structure matched with JCPDS-784486. No rutile peak appeared in either XRD results due to insufficient sintered temperature. Generally, rutile is more densely packed and thermodynamically stable than anatase [79], whereas the latter is

considered the more photoactive form of TiO₂. The lattice constants were a=3.7993 +/- 0.0009 and c=9.4983 +/- 0.004 for NTTF and a=3.7806 +/- 0.002 and c=9.4893 +/- 0.009 and the obtained values match closely with the identified structure.

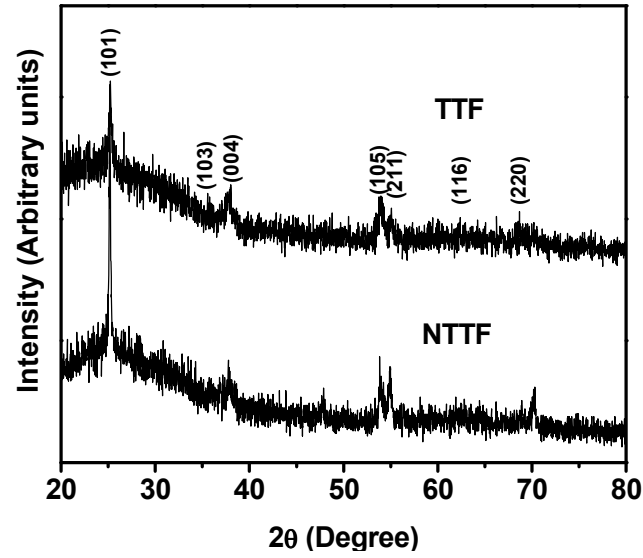


Figure 2.2. XRD patterns of TTF and NTTF (Courtesy of Emre Yassitepe).

The absorption coefficient of the thin films was calculated with the following formula [80];

$$\alpha(h\nu) = -\frac{1}{d} \ln \left(\frac{T}{(1-R)^2} \right) \quad (3.21)$$

Where α is the absorption coefficient, d is the thickness of the film, for T is transmission a particular wavelength, and R is the reflectance characteristics of the film.

$$\alpha(h\nu) \propto \frac{(h\nu - E_G)^n}{h\nu} \quad (3.22)$$

The optical band gap was calculated by plotting $(\alpha \times h\nu)^n$ vs. $h\nu$ where n is 0.5 for indirect and 1 for direct band gap materials. The doping effect can be seen in the band gap characterization results. From figure 2.2, both TTF and NTTF showed the characteristic band gap of 3.2 eV, which corresponds to anatase phase in titanium dioxide nanomaterial. Furthermore, NTTF showed a secondary slope at 2.0 eV, which was attributed to the additional states due to the nitrogen doping [81-84]. As demonstrated in the inset plot in figure 2.3, the absorbance shoulders for NTTF exhibited high absorbance in longer wavelength at 595 nm, which indicated that NTTF can be excited in visible region. The significant absorbance for visible light can be attributed to the O–Ti–N linkage, leading to the narrowing of energy band gap [84, 85]. This phenomenon illustrated the formation of an intra-band gap located above the valence band, due to the interstitial introduction of nitride into the oxide lattice and/or to substitution of oxide centers by nitride centers [86].

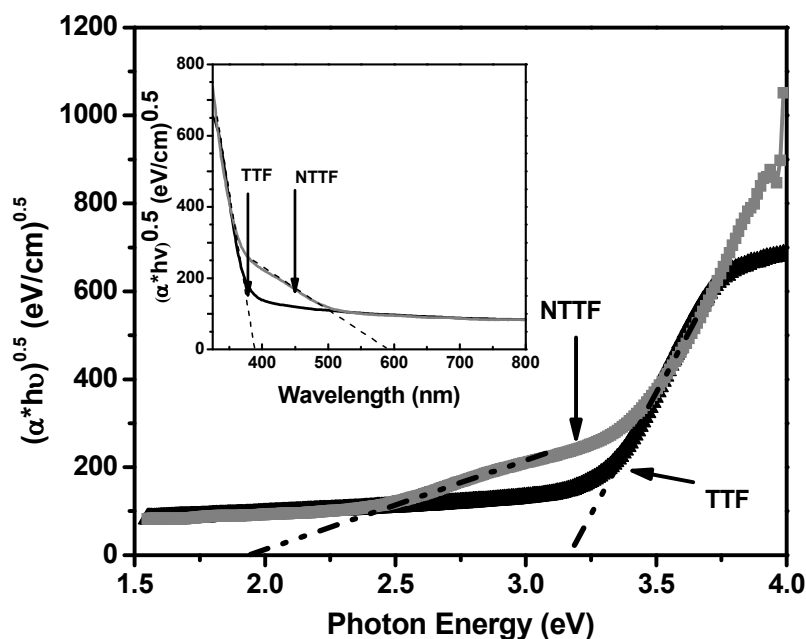


Figure 2.3. Optical band gap characterization of TTF and NTTF. Inset plot shows the Uv-vis absorbance of TTF and NTTF (Courtesy of Emre Yassitepe).

Figure 2.4 showed the SEM images collected for surface and cross section of the TTF and NTTF. The cross sections showed continuous and uniform area with columnar grains with an average thickness of 545 and 640nm for NTTF and TTF, respectively. This illustrated the nitrogen-doped TiO_2 attached firmly and spread evenly on the ITO glass, which is beneficial for wide application. The surface images showed that TTF (100 nm) had a larger grain size than NTTF (60 nm), and had a rougher surface. The differences resulted from the different gases employed in the synthesis procedure. Only oxygen gas was employed in the TTF synthesized process,

however a blend gas with a mixed ratio of 4:1 for nitrogen and oxygen was purged into the system for NTTF synthesis. The non-uniformity comes from the PLD technique due to the molecular breaking of the bonds. Similar results were observed for carbon-doped titanium dioxide thin film in our previous study as well [22].

In order to analyze chemical bonding states (and concentration of Nitrogen) near the film surface, two XPS high resolution-scan spectra, Ti 2p (Figure 2.5a), and N 1s (Figure 2.5b), were investigated. Figure 2.5a showed the high resolution result of XPS spectra for Ti 2p. It could be seen that Ti 2p spectra of NTTF consists of two peaks at around 459.5 eV (Ti 2p_{3/2}) and 465.3 eV (Ti 2p_{1/2}). Ti 2p region showed that Ti is in +4 state was confirmed by the oxidation of Ti to TiO₂. A Ti +3 state is also observed due to the vacancies creating by the PLD procedure and nitrogen doping. In contrast to chemical-based synthesis (i.e. sol-gel and MOCVD), multi-valance Ti species are usually created during the PLD deposition process [77]. The N1s spectra showed the Ti–O–N bond and N–Ti–O bond at 400 eV and 396.5 eV, respectively. The appearance of N 1S spectra in NTTF provides evidence that nitrogen were successfully doped into by using PLD method. The nitrogen concentration was 3% in the NTTF from XPS analysis. From XPS and UV-VIS results, we can see the band gap reduction by creating the additional states with Nitrogen doping.

Notably, the colors of samples sintered at 600 °C were yellow, which was indicative of the successful doping of N into TiO₂ lattice and exhibits a good absorbance of visible light [82, 84, 87]. The phenomenon was consistent to the results of XPS and UV-vis analysis as well.

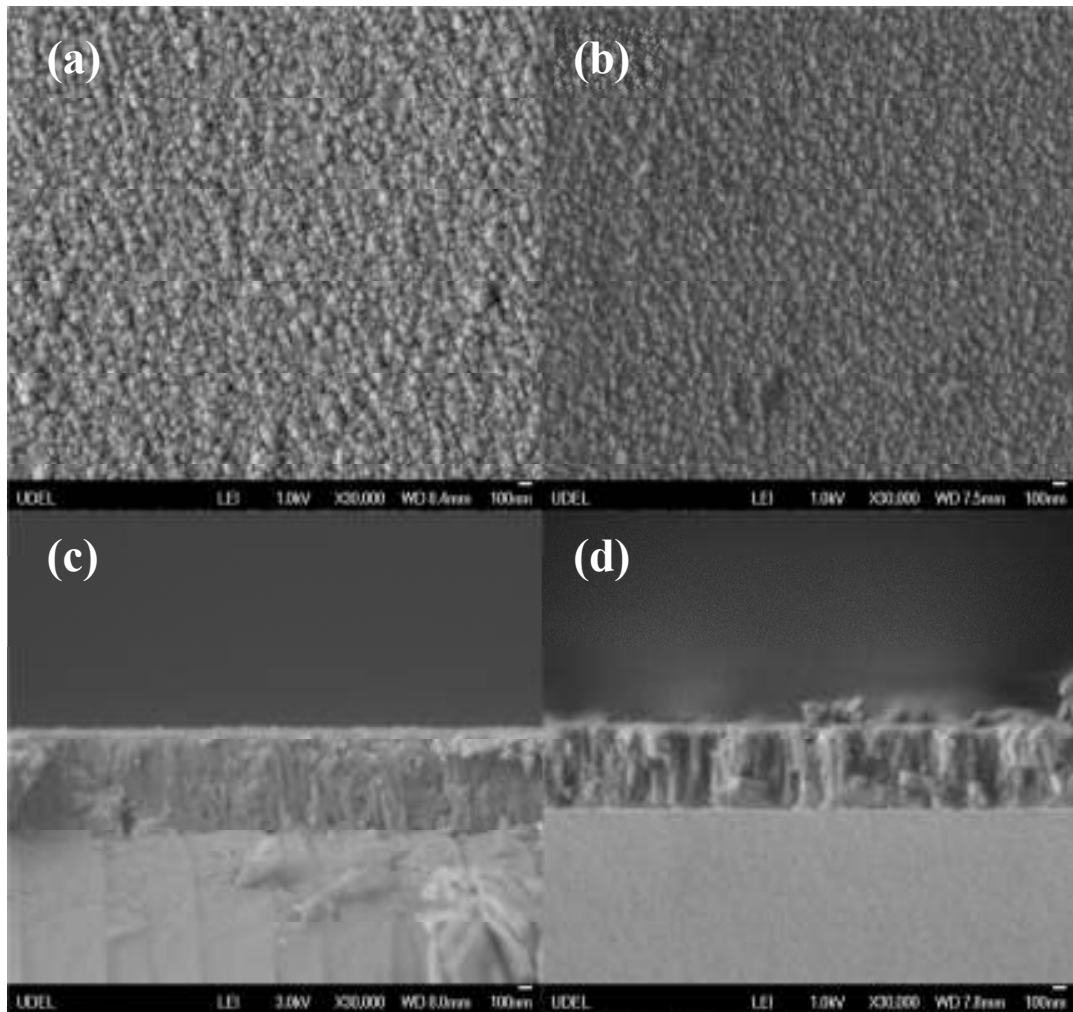


Figure 2.4. SEM images of the surface of (a) TTF, (b) NTTF; cross-section images for (c) TTF and (d) NTTF (Courtesy of Emre Yassitepe).

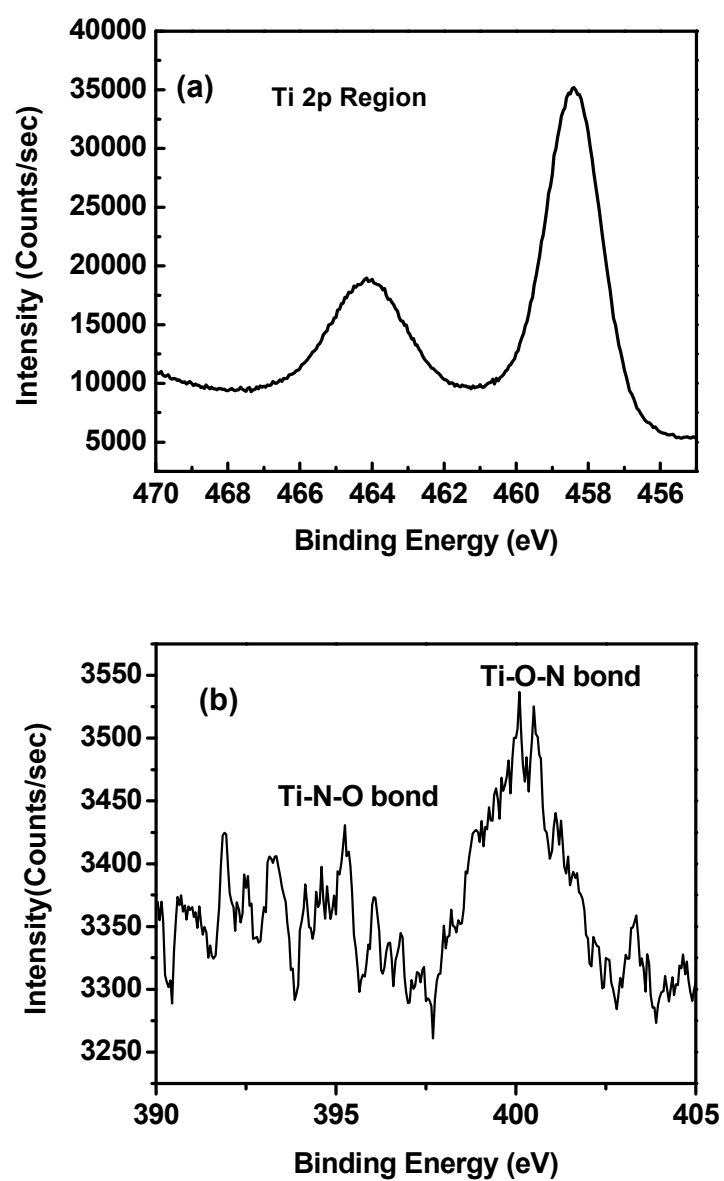


Figure 2.5. High resolution XPS spectra for (a) Ti 2p, and (b) N1s region of NTTF (Courtesy of Emre Yassitepe).

2.3.2. Photoelectrochemical activities of NTTF

The incident photon conversion efficiency IPCE (λ) test was performed to examine the photoelectrochemical efficiency of NTTF. The IPCE (λ) is defined as the number of electrons transferred per incident photon (equation 3)

$$IPCE (\%) = \frac{J_{sc}(\lambda)}{eI_{inc}(\lambda)} = \left[1242 \frac{J_{sc}(A/cm^2)}{e\lambda(nm)I_{inc}(W/cm^2)} \right] \times 100 \quad (3.23)$$

where the $J_{sc}(\lambda)$ is short-circuit photocurrent density under monochromatic light (A/cm^2), e is the electron charge (Coulomb), and $I_{inc}(\lambda)$ is the incident photon flux (W/cm^2). This method provides more information than optical absorption, due to the fact that surface morphology and mass transfer limitation effect are not fully taken into account in the latter method. The IPCE (λ) is a function of incident wavelength for a particular semiconductor photoelectrode as a quantum efficiency profile measurement. When applying a certain photon energy/wavelength, the obtained quantum efficiency represents the energy differences between the local electronic states and the conduction band minimum. Therefore, if there is no significant change in energy position of the conduction band minimum, the edge of the IPCE (λ) spectrum is qualitatively proportional to the density of states for the valance band maximum. In other words, the onset of the IPCE (λ) spectrum is similar to the wavelength of bandgap threshold (λ_{bg}) of a particular semiconductor.

The IPCE (λ) of NTTF were investigated at 0.3, 0.5, 0.7, 1.0, 1.5 and 2.0 V, and also under 300 to 425 nm with every 25 nm interval of irradiation. As shown in figure 2.6, the IPCE (λ) value of NTTF increased with the increasing external

potential. The highest photoresponse was obtained at 325 nm i.e., the maximum value of 26.77% was observed at irradiation of 325 nm and a bias potential of 2.0 V (Table 2.2). Although the UV-vis results provide evidence that NTTF can be excited in visible light region, the IPCE results showed a better photoelectro response of NTTF at shorter irradiation wavelength. This might be that shorter wavelength of the illumination always combine higher light energy. Higher light energy accompanies greater photon kinetic energy, which facilitates their movement. The IPCE for pure TiO₂ film was also calculated under the same irradiation and a bias potential of 0.75 V in our previous study. In contrast to NTTF whose photocurrent was 1.142 mA at 425 nm, the pure TiO₂ thin film generated photocurrent almost disappeared at 400 nm [22]. This illustrated that NTTF has better visible light response than pure TiO₂ thin film. Notably, the IPCE (λ) spectrum performed similar trends with the UV-vis diffuse reflectance absorption, and both showed two adsorption edges as evidence of that the IPCE (λ) function considers the effect of surface morphology and mass transfer limitation on the determination of band gap.

Table 2.2. IPCE (%) and photocurrents at various bias potential.

V_{bias} (vs. SCE, V)	0.3	0.5	0.7	1.0	1.5	2.0
Darkcurrent (mA)	0.023	0.160	0.292	0.413	0.517	0.607
Photocurrent (mA)	0.095	0.358	0.515	0.75	1.099	1.202
Light intensity (mW/cm²)	7.6	7.6	7.6	7.6	7.6	7.6
IPCE (%)	2.93	8.06	9.08	13.72	23.70	26.77

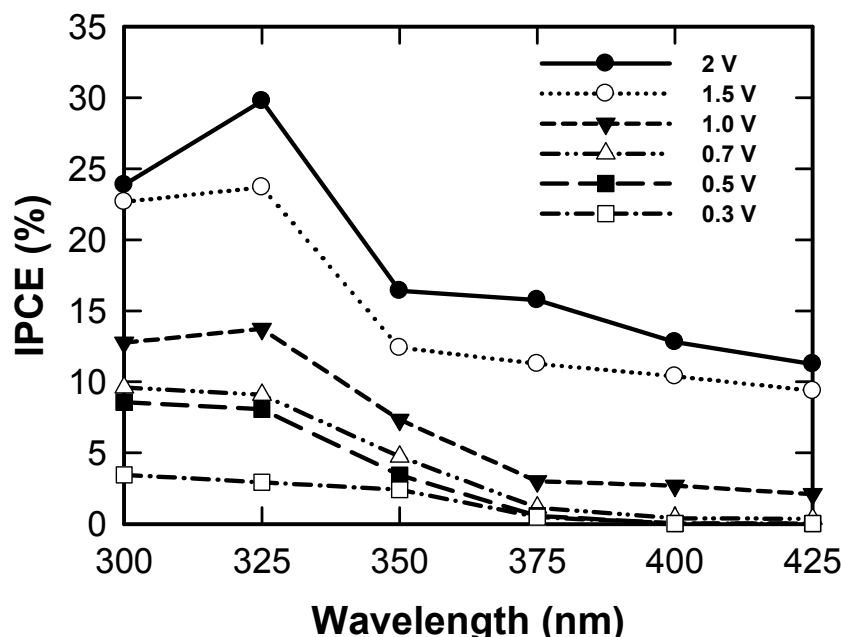


Figure 2.6. IPCE (%) versus wavelength (300–425 nm) as a function of bias potential in 0.1 M NaCl electrolyte. Experimental conditions: anode = NTTF; reference electrode = SCE; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO₃ (cathode); pH = 7.0 (anode); pH = 8.3 (cathode); temperature = 298 K; light source = Monochromatic excitation source (Model RF-5301, Shimadzu, Japan; 7.6mW/cm).

2.3.3. Current-Potential Curves of N-doped TiO₂ Thin Film

The current-potential curves of the NTTF photoanode in a H-type PEC system were recorded at 298 K. The potential was scanned at a sweep of 50 mV s⁻¹. The electrolyte is 1 ppm MO in 0.1 M NaCl in the anode and 0.1 M KHCO₃ in the cathode. Figure 2.7 shows the typical I-V curves. The applied voltage in this study started at 0 and went up to 2 V vs SCE, in contrast to most PEC CO₂ reduction studies

in order to focus on the electrons generated by the photoanode. Under illumination, the onset potential of the photocurrent was approximately 1.5 V (vs. SCE). The maximum current was around 0.65 mA at 2 V (vs. SCE) in the NTTF PEC system. This indicates that the photocurrent generated by the NTTF photoanode could be effectively driven to the counter electrode by this positive potential, which would be beneficial to the separation of photogenerated holes and electrons. According to the previous study, the greater the increase in bias potential, a kind of driving force, the greater the decrease in recombination of electrons and holes. Meanwhile, applying a larger external potential can lead to more electrons to participate in electrochemical oxidations reaction in the anodic chamber.

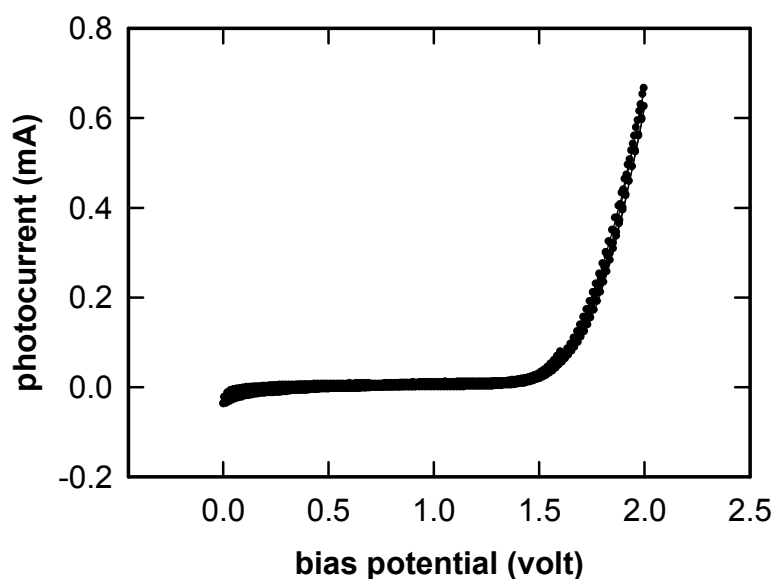
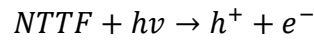


Figure 2.7. Cyclic voltammery scans with NTTF working electrode in 1 ppm MO. The light source used was 100 W Xe lamp (3.12 mWcm^{-2}) and electrolyte was 0.1 M NaCl in the anode chamber and 0.1 M KHCO_3 in the cathode chamber.

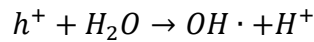
2.3.4. Photoelectrochemical Reduction Mechanism of CO₂

N-doped TiO₂ thin film is a kind of semiconductor material. Photogenerated electrons and holes will form on the surface of NTTF with a sufficient photonic energy and an appropriate wavelength. However, the electrons and holes that are formed upon solar light irradiation will undergo recombination rapidly, estimated at a rate of $(3.2 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [88]. Hole-electron recombination will decrease the overall photocatalysis quantum yield. Moreover, since holes are strong oxidants, they will tend to oxidize photocatalytic products such as methanol or organic acids back to CO₂. Therefore, the PEC method which combines electrooxidation and photocatalysis, was applied to minimize the recombination effect and to separate the electrons and the holes by adding a bias potential between the anode and the cathode.

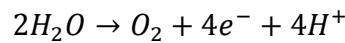
In the anode, holes and electrons were generated when the NTTF was excited by visible light.



The holes first react with water absorbed on the NTTF, resulting in the production of hydroxyl radicals and hydrogen ions.



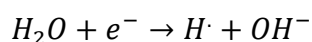
As the bias potential was applied, water in the anode was oxidized to oxygen, electrons and H⁺ according to the following reaction:



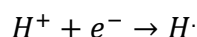
Notably, the electrons generated in the anode are driven to the cathode by the potentiostat. This phenomenon can not only promote the reduction reaction in the cathode but also decrease the recombination effect in the anode. In addition, the hydroxyl radical and oxygen play two important roles in the oxidation reaction in the anode chamber. The hydroxyl radical ($E^\circ = 2.72 \text{ V}$), a strong oxidant in photo

activated NTTF, has been supported from the formation of hydroxylated intermediates during the PEC degradation of aqueous pollutants. In addition, oxygen derived from the electrolysis of water is advantageous for pollutant oxidation. The protons pass through the cation exchange membrane to the cathodic chamber to balance the ionic conditions.

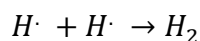
In the cathode, the electrolysis of water leads to formation of hydrogen radicals ($H\cdot$) and OH^- .



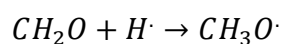
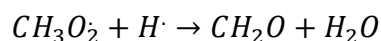
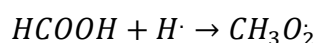
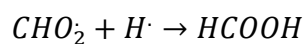
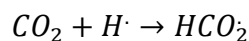
The absence of dissolved oxygen, can only favor the reduction of proton to form radicals, such as:

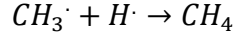
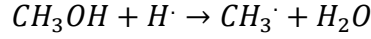
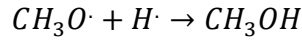


The obtained hydrogen radicals will then combine rapidly to form hydrogen, which is a useful energy.



This well-known water splitting reaction was applied by the use of PEC methods to generate hydrogen [22, 89-92]. In addition, the hydrogen radical, a reductant, consequently dominated each step of CO_2 reduction reaction to form formic acid ($HCOOH$), formaldehyde ($HCHO$), methanol (CH_3OH) and methane (CH_4) [7, 13, 76].





Another possible pathway of CO₂ reduction is: CO₂ → CO → C · → CH₂ → CH₄, to yield the end product of CH₄ through different intermediates. This has been proposed based on the Rectisol process and also on electrolytic reduction of CO₂ [66, 93, 94].

2.3.5. Kinetic Study of PEC Reduction of CO₂

The assumed CO₂ reduction reactions for the kinetic study in NTTF PEC system is a series reaction which can describe as:



The aqueous CO₂ react with hydrogen radical to form formic acid, formaldehyde, methanol, and methane in series. The intermediates generated in each step are ignored for the model simulation because they are not stable and react rapidly with hydrogen radicals. The series reactions were solved by the differential solution and the kinetic constants (k₁–k₄) were solved SSR method. Moreover, experimental CO₂ reductions of HCOOH, HCOH, CH₃OH, and CH₄ were conducted for comparison.

The consumption of CO₂ in the system can be represented by:

$$\frac{d[CO_2]}{dt} = -k_1[CO_2] \quad (2.1)$$

Therefore, the kinetic equation can be written as follows,

$$[CO_2] = [CO_2]_0 e^{-k_1 t} \quad (2.2)$$

where [CO₂]₀ represents the initial carbon dioxide concentration in the cathode chamber including both gaseous and aqueous samples; *t* is the reaction time and *k₁* is the rate constant for CO₂ consumption.

According to the series reaction, the formic acid concentration is related to CO_2 consumption and formaldehyde generation, described as:

$$\frac{d[\text{HCOOH}]}{dt} = k_1[\text{CO}_2] - k_2[\text{HCOOH}] \quad (2.3)$$

Then, the kinetic equation can be solved as follow,

$$[\text{HCOOH}] = [\text{HCOOH}]_0 e^{-k_2 t} + \frac{k_1[\text{CO}_2]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (2.4)$$

where $[\text{HCOOH}]_0$ is the initial formic acid concentration in the system (herein is zero), and k_2 is the rate constant for formic acid.

The formic acid would then reduce to form the formaldehyde as:

$$\frac{d[\text{HCOH}]}{dt} = k_2[\text{HCOOH}] - k_3[\text{HCOH}] \quad (2.5)$$

The differential solution for the above equation should then be:

$$\begin{aligned} [\text{HCOH}] = & [\text{HCOH}]_0 e^{-k_3 t} + \frac{k_2[\text{HCOOH}]_0}{k_3 - k_2} (e^{-k_2 t} - e^{-k_3 t}) \\ & + \frac{k_2 k_1[\text{CO}_2]_0}{k_3 - k_2} \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} - \frac{e^{-k_1 t} - e^{-k_3 t}}{k_3 - k_1} \right) \end{aligned} \quad (2.6)$$

where $[\text{HCOH}]_0$ is the initial formaldehyde concentration and k_3 is the rate constant for formaldehyde.

The methanol reduction reaction in the series reaction can be described as:

$$\frac{d[\text{CH}_3\text{OH}]}{dt} = k_3[\text{HCOH}] - k_4[\text{CH}_3\text{OH}] \quad (2.7)$$

The solution for the equation is as follows:

$$[\text{CH}_3\text{OH}] = [\text{CH}_3\text{OH}]_0 e^{-k_4 t} + \frac{k_3[\text{HCOH}]_0}{k_4 - k_3} (e^{-k_3 t} - e^{-k_4 t})$$

$$\begin{aligned}
& + \frac{k_3 k_2 [HCOOH]_0}{k_3 - k_2} \left(\frac{e^{-k_2 t} - e^{-k_4 t}}{k_4 - k_2} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right) \\
& + \frac{k_3 k_2 k_1 [CO_2]_0}{(k_2 - k_1)(k_3 - k_1)} \left(\frac{e^{-k_1 t} - e^{-k_4 t}}{k_4 - k_1} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right) \\
& - \frac{k_3 k_2 k_1 [CO_2]_0}{(k_2 - k_1)(k_3 - k_2)} \left(\frac{e^{-k_2 t} - e^{-k_4 t}}{k_4 - k_2} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right)
\end{aligned} \tag{2.8}$$

where $[CH_3OH]_0$ is the initial methanol concentration in the system, and k_4 is the rate constant for methanol.

Methane, the final product, comes from the reaction of $CH_3\cdot$ with $H\cdot$. There is no further product of the series reaction in the assumption. So, the process of methane generation can be described as:

$$\frac{d[CH_4]}{dt} = k_4 [CH_3OH] \tag{2.9}$$

The differential solution is given as follows:

$$\begin{aligned}
[CH_4] = & k_1 k_2 k_3 [CO_2]_0 \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{(k_4 - k_3)(k_3 - k_2)(k_2 - k_1)} \right. \\
& - \frac{e^{-k_1 t} - e^{-k_3 t}}{(k_4 - k_3)(k_3 - k_2)(k_3 - k_1)} - \frac{e^{-k_1 t} - e^{-k_2 t}}{(k_4 - k_3)(k_4 - k_2)(k_2 - k_1)} \\
& + \frac{e^{-k_1 t} - e^{-k_4 t}}{(k_4 - k_3)(k_4 - k_2)(k_4 - k_1)} + \frac{e^{-k_1 t} - e^{-k_2 t}}{k_3(k_3 - k_2)(k_2 - k_1)} \\
& \left. - \frac{e^{-k_1 t} - e^{-k_3 t}}{k_3(k_3 - k_2)(k_3 - k_1)} + \frac{e^{-k_1 t} - e^{-k_2 t}}{k_3 k_2(k_2 - k_1)} + \frac{e^{-k_1 t} - 1}{k_3 k_2 k_1} \right)
\end{aligned} \tag{2.10}$$

where k_4 is the rate constant for methane formation.

Figure 2.8 compares experimental and simulated results for PEC CO_2 reduction products. The electrolyte is 5 ppm methyl orange with added 0.1 M NaCl to increase the conductivity in the anode chamber. The catholyte is 0.1 M $KHCO_3$

solution (initial pH = 8.3) bubbled with CO₂ gas until saturated (pH = 6.8). The photocurrent was 0.5 mA, generated from the NTTF photoanode at a 2.0 V bias potential. Formic acid, formaldehyde and methanol were detected in liquid phase while the methane was detected in gas phase. Figures 2.8 (a)–(c) illustrate the measured HCOOH, HCOH and CH₃OH concentrations increased apparently in the first three hours and then went flat after the fourth hour. However, the measured CH₄ increased continuously from the second hour, as seen in figure 2.8(d). The trends in measured values were consistent with simulated results for HCOOH, HCOH, CH₃OH and CH₄. The performance of the model was obtained relative to the measurements using the index of agreement (IOA) [95, 96],

$$d_1 = 1 - \frac{\sum_{i=1}^N (|P_i - O_i|)}{\sum_{i=1}^N (|P_i - \bar{O}| + |O_i - \bar{O}|)} \quad (2.11)$$

where d_1 is the value of IOA; P_i and O_i are the predicted and measured values, respectively, with a sample size N ; and $\bar{O}$ is the average of all measured data. Table 2.3 summarized the statistic data for the comparison of measured and simulated HCOOH, HCOH, CH₃OH and CH₄. The agreement between prediction and measurement is regarded as good when IOA exceeds 0.5 [95]. The rate constants were calculated as 1.30×10^{-8} , 4.26×10^{-6} , 1.68×10^{-5} and 4.43×10^{-6} (s⁻¹/cm²) for k_1 , k_2 , k_3 and k_4 respectively. Notably, k_1 is a thousand times smaller than the others due to the relative high initial carbon dioxide concentration (0.13M) in the cathodic chamber.

Table 2.3. The rate constant (k) of photoelectrochemical reduction of CO₂ at Cu electrode in KHCO₃ (0.1 M) electrolyte

	Kinetic rate constant		IOA
	k, (s ⁻¹ /cm ²)	k, (s ⁻¹)	
k ₁	1.30 × 10 ⁻⁸	6.68 × 10 ⁻⁷	0.87
k ₂	4.26 × 10 ⁻⁶	2.18 × 10 ⁻⁴	0.92
k ₃	1.68 × 10 ⁻⁵	8.62 × 10 ⁻⁴	0.94
k ₄	4.43 × 10 ⁻⁶	2.27 × 10 ⁻⁴	0.96

Catholyte: KHCO₃ (0.1 M), anolyte: NaCl (0.1 M), temperature 298.15 K, potential 2.0 V vs SCE.

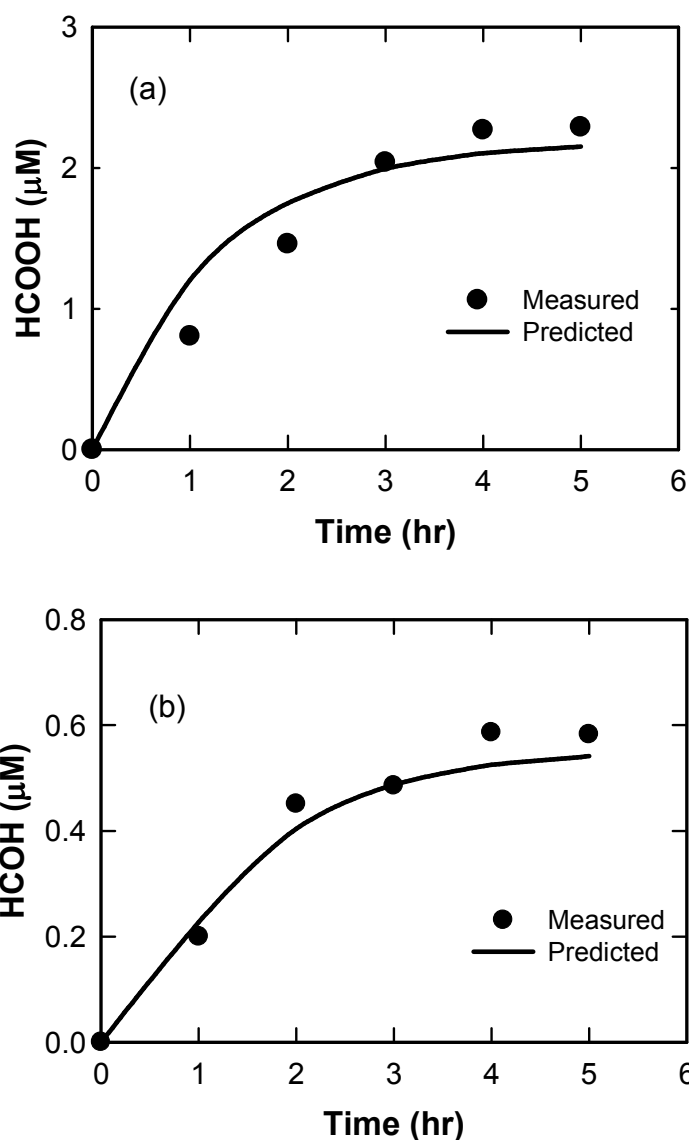


Figure 2.8. Comparison of experimental data with predicted concentrations for (a) HCOOH , (b) HCOH , (c) CH_3OH , and (d) CH_4 based on differential first-order models. Experimental conditions: anode = NTTF; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO_3 (cathode); pH = 6.0 (anode); pH = 6.8 (cathode); temperature = 298.15 K; light source = Monochromatic excitation source (Model RF-5301, Shimadzu, Japan; 7.6 mW/cm)

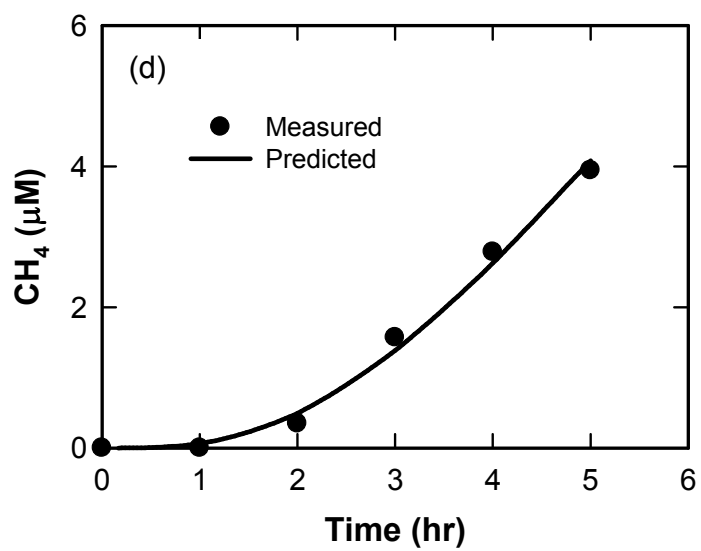
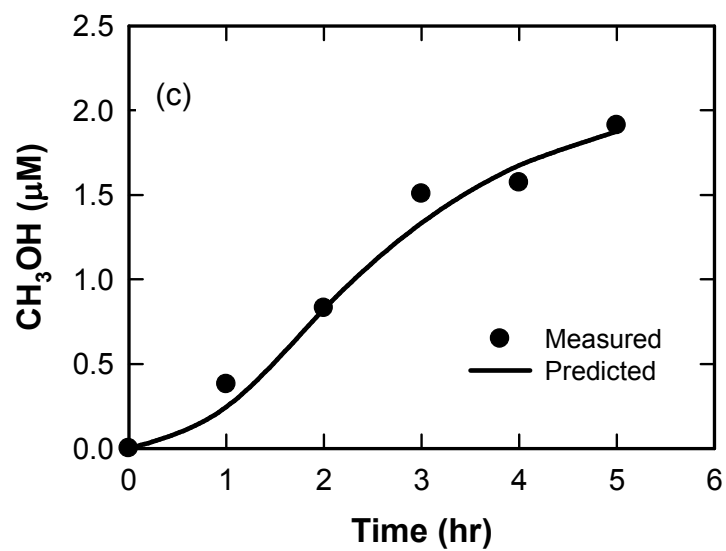


Figure 2.8. continued

2.3.6. Faradaic Efficiency of CO₂ Reduction Products in PEC Process

The Faradaic efficiencies for the products of photoelectrochemical reduction of CO₂ on Cu in KHCO₃-based electrolyte at 298 K are shown in Table 2.4. Formic acid, formaldehyde, methanol and methane were detected as CO₂ reduction products, and hydrogen gas was detected as the product of water splitting. The photocurrent was 4 ($\pm$ 1) mA at the bias potential of 2 V (vs. SCE) under 100 W irradiation (Xe lamp, 3.12mWcm⁻²). The highest Faradaic efficiencies were 5.01, 1.04, 5.41 and 7.83% for HCOOH, HCOH, CH₃OH, and CH₄, respectively. In addition, hydrogen reached its highest Faradaic efficiency (50.34%) at the fifth hour. Interestingly, Faradaic efficiencies decreased with the increasing reaction time for HCOOH, HCOH and CH₃OH. On the contrary, Faradaic efficiencies of CH₄ and H₂ increased with increasing reaction time. These phenomena correspond to both the simulated and measured results in figure 2.8. The concentrations of HCOOH, HCOH and CH₃OH approached a constant value when the formation and consumption reactions of each product achieved a balance. Therefore, as CO₂ continuously reduced in the system, the final product of CH₄ increases consecutively. Furthermore, more H⁺ were allowed to form H₂, which dominate the Faradaic efficiency in our CO₂ reduction PEC system at the last hour.

Table 2.4. Faradaic efficiency (%) of CO₂ reduction products in PEC process (in 0.1 M KHCO₃ electrolyte)

Time (hr)	HCOOH	HCOH	CH ₃ OH	CH ₄	H ₂	Total
1	5.01	1.04	5.41	0.00	0.00	11.46
2	4.44	0.69	5.02	2.00	10.90	23.05
3	4.52	0.48	4.48	2.26	14.11	25.85
4	3.30	0.46	3.43	6.35	26.15	39.69
5	2.60	0.39	3.26	7.83	50.34	64.42

2.3.7. Effect of CO₂ Solubility on CO₂ Reduction

Methanol is a better solvent for CO₂ than water, particularly at low temperatures. The solubility of CO₂ in methanol is about four times that in water at ambient temperature and eight times that in water at temperatures below 273 K. Therefore, methanol has been used as a physical absorbent of carbon dioxide in the Rectisol method at 243–263 K [93]. It is conceivable that higher dissolved CO₂ concentrations in the electrolyte accompany more CO₂ reduction products. However, to the best of our knowledge, there is no report about the effects of CO₂ initial concentration on CO₂ reduction in a NTTF two-chamber PEC system. Thus, to investigate the effect of CO₂ solubility on PEC CO₂ reduction, three concentrations, i.e., 0, 20, and 40%, of methanol dissolved with 0.1 M KHCO₃ electrolyte were applied. All the electrolytes in the cathode chamber were bubbled with 99.99% CO₂ gas for 90 minutes. Figure 2.9 illustrates the influence of CO₂ solubility on the yield of HCOOH, HCOH, CH₄, and H₂. Notably, CH₃OH is not measurable due to the high CH₃OH background concentration in a methanol-based electrolyte. The trends of CO₂ reduction products for three different concentrations of methanol-based electrolytes were similar. Both HCOOH and HCOH concentrations approached a constant value, which represented a balance of formation and consumption reactions. In addition, methane was generated directly in the first reaction hour for 20 and 40% methanol-based electrolytes; however, it did not formed rapidly until the third hour for 0% methanol-based electrolyte. This might be due to some CH₄ forming directly from CH₃OH, which was used as a solvent for CO₂ dissolution in the methanol-based electrolyte. From figure 2.9, the yields of formic acid, formaldehyde and methane in 40% methanol-based electrolyte were approximately 12, 3, and 2.7 times higher than that in 0% methanol-based electrolyte. These results demonstrate that higher dissolved

CO₂ concentrations can enhance the formation of CO₂ reduction products. Moreover, hydrogen, which would compete with CO₂ reduction products for electrons, decreases with increasing methanol concentration in the electrolyte (see figure 2.9 (d)). Kaneco *et al.* studied the electrochemical reduction of CO₂ in CsOH/methanol electrolyte on the Cu electrode and found that hydrogen production can be successfully suppressed in a methanol-based electrolyte. The current efficiency for hydrogen formation on a Cu electrode at 243 K in CsOH/methanol electrolyte was suppressed to below 23% [54].

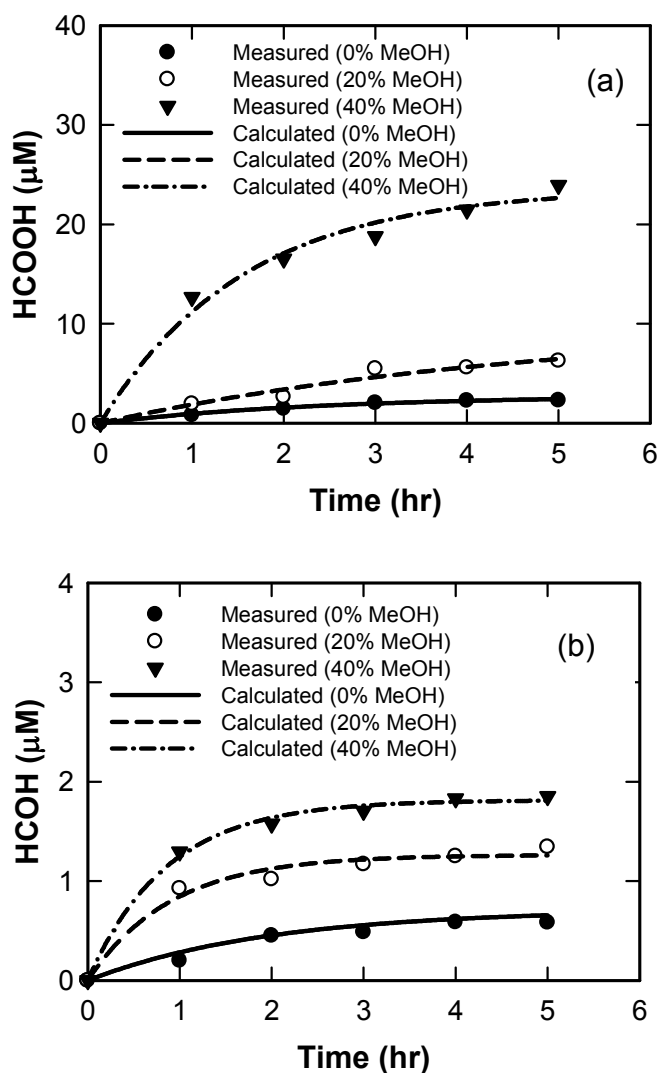


Figure 2.9. The effect of the methanol concentration in the catholyte on photoelectrochemical reduction of CO_2 with (a) HCOOH , (b) HCOH , (c) CH_4 , and (d) H_2 concentrations predicted based on differential first-order model. Calculated lines were fitted using Sigma Plot. Experimental conditions: anode = NTTF; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO_3 /0 to 40% methanol (cathode); pH = 6.0 (anode); pH = 6.8 (cathode); temperature = 298.15 K; light source = Xe lamp (3.12 mW/cm)

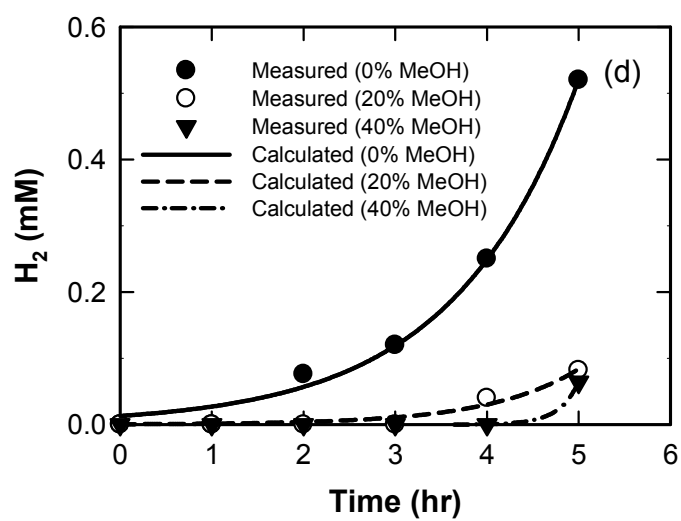
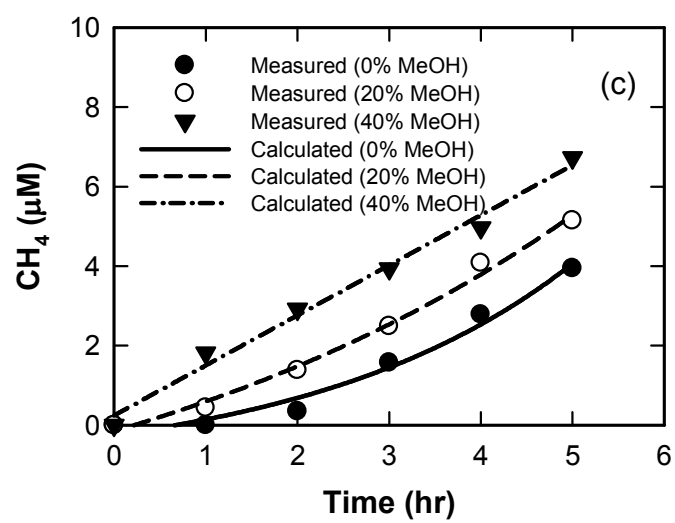


Figure 2.9. continued

2.3.8. Degradation of MO

Four MO removal processes, namely, PEC, photocatalytic (PC), electrochemical [97] and direct photolysis (P) processes were conducted to evaluate the degradation efficiency. The PEC, PC and photolysis experiment were examined at the illumination of 100 W Xe lamp with 3.12 mW/cm^2 . Applied voltage in PEC and EC process was 2.0V (vs. SCE), at which, both CV (figure 2.7) and IPCE results showed the best response of photocurrent-bias potential. As shown in figure 2.10, PEC process was the most efficient way to degrade MO among four methods mentioned above. The complete removal of 1ppm MO was observed after 40 min, while only 14.9, 36.3 and 5.1% of the MO removal was achieved for the PC, EC and P process at the same irradiation time. It was comprehensible that PEC method provided the most powerful way to degrade MO due to the combination of electrochemical oxidation and photocatalysis. Zhao *et al.* [98] successfully demonstrated the synergetic effect of combining electro-oxidation and photolysis by using porous ZnWO_4 photoanode to oxidize Rh-B. The results showed that when the bias potential was greater than 1.3V, indirect electron-oxidation of Rh-B occurred with the largest synergetic effect. Similar results were also shown in this study. As the bias potential was applied, the photocatalytic degradation of MO was enhanced by promoting the separation and transfer of photogenerated electrons and holes. This enhanced not only the electrochemical oxidation but also the photocatalytic oxidation. The effect of bias potentials and the MO degradation mechanism for PEC process will be discussed in the following sections. For the comparison of PC and EC method for MO degradation, 19.5 and 47.0% MO was removed by PC and EC method, respectively. The degradation rate constant was $1.50 \times 10^{-7} \text{ s}^{-1}/\text{cm}^2$ for EC method and $4.32 \times 10^{-7} \text{ s}^{-1}/\text{cm}^2$ for PC method. The applied voltage in EC method is a key point regarding the

degradation efficiency. For example, Zhao *et al.* [99] applied γ -Bi₂MoO₆ film electrode to examine oxidation efficiency of Azo dye via photocatalysis degradation (irradiated by 150 W Xe lamp) and electro-oxidation (under bias potential of 3.0 V vs. SCE). Results showed that EC method had better efficiency than PC method. However, Hou *et al.* [100] used TiO₂ film onto activated carbon fibers (TiO₂/ACF) to compare their electrochemical and photocatalysis abilities on oxidation of Acid Orange II. PC (irradiated by 15 W UV₂₅₄ lamp) and EC (under bias potential of 0.5 V vs. SCE) method removed 77.8 and 51.1% AOII in 180 minutes, respectively. Above results illustrated that, as the applied bias potential was below the redox potential of the target compound, the increasing bias potential could increase the photocatalytic ability by promoting the separation and transfer of photogenerated holes and electrons. In contrast, the applied bias potential, beyond the redox potential of target compound, not only can separate the holes and electrons but also can directly electrolyze target compound [98]. Figure 2.7 shows the CV results for the NTTF in 1ppm MO with 0.1 M NaCl solution under irradiation (100W Xe lamp). When the bias potential exceeded 1.6V, the current increased largely, this may be due to the electro-oxidation of MO plus the oxygen evolution. In addition, the photocurrent was potential dependent. It increased as the applied potential was scanned toward more positive potential, especially at potentials larger than 1.6V, and this trend gradually reached a maximum photocurrent (at 2.0 V). This represents that the photocurrent generated from the NTTF photoanode could be effectively driven to the counter electrode by this positive potential, which would be beneficial to charge separation. In two-chamber PEC system, applying potentials greater than NTTF flat band potential under illumination condition could transfer the photogenerated current to an external circuit to the

cathode. This may increase the photogenerated active species on the surface of photoanode by decreasing the recombination rate of photogenerated holes and electrons. Moreover, no vibrational concentration was observed in the presence of NTTF electrode without light illumination. This illustrates that the adsorption effect can be ignored during the reaction process.

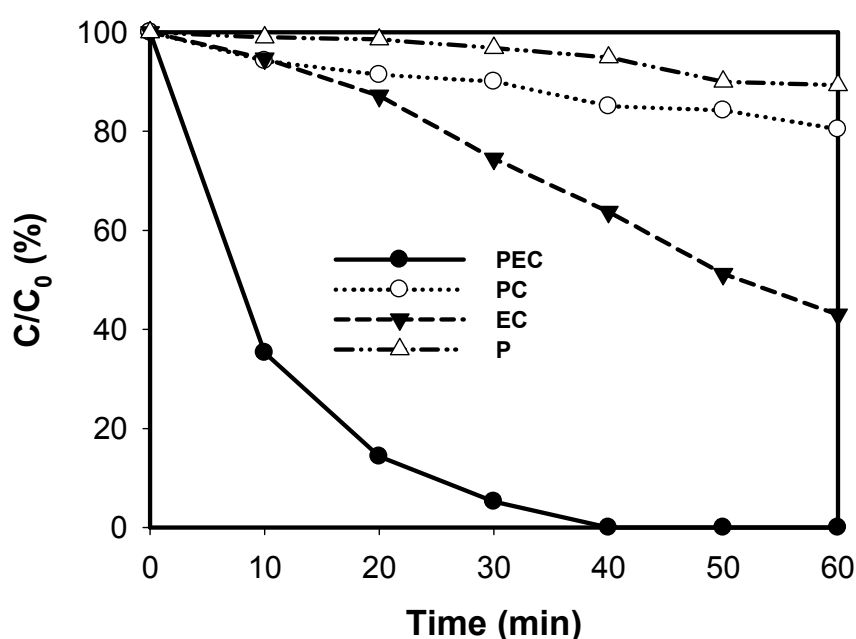


Figure 2.10. Comparing the treatment of MO by PEC, PC, EC, and P methods. Experimental conditions: anode = NTTF; cathode = copper; initial concentration of MO was 1 ppm; light source = 3.12 mWcm^{-2} (100 W Xe lamp); anode = NTTF; reference electrode = SCE; cathode = copper; bias potential = 2 volt (vs. SCE); pH = 6.0 (anode); pH = 6.8 (cathode); electrolyte = 1 ppm MO in 0.1 M NaCl (anode); electrolyte = 0.1 M KHCO_3 (cathode); temperature = 298 K.

2.3.9. Effect of Bias Potential

Various external potentials of 0, 0.5, 1.0, 1.5 and 2.0 V were applied to evaluate the NTTF electrode activity by the study of PEC degradation of MO. As shown in figure 2.11, the degradation rate of MO increases as a function of bias potential. It was clearly observed that the applied bias potential of 2.0 V provided the most powerful way to degrade the MO in aqueous solution. The complete removal of MO was observed after 40 min, while only 78.3 and 36.3% of the MO degradation were obtained at the applied bias potential of 0.5 and 0 V, respectively. Furthermore, it was found that the experimental data approximately fit a pseudo-first-order kinetic model with the linear transforms $\ln(C_0/C) = kt$. As shown in Table 2.5, the reaction rate for 2V applied bias potential ($4.32 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$) was about 10 times higher than that in 0 V condition ($4.32 \times 10^{-7} \text{ s}^{-1}/\text{cm}^2$) at the same illumination. Since the light intensity was in the equivalent condition in these two cases, the photocatalysis should be the same. Therefore, the difference may be due to two main reasons. The first one is the higher external the potential that was applied, the higher the current that was generated. The electrons can operate the indirect electro-oxidation reaction on MO as the reaction $H_2O \rightarrow O_2 + 4H^+ + 4e^-$, where O_2 is an oxidant. The second reason is that higher external potential can enhance the separation of photogenerated holes and electrons. This separation allowed more holes, which are strong oxidants, to oxidize the MO in aqueous solution. The total electrons (e_T^-) in the PEC system can be described as:

$$e_T^- = e_{NTTF}^- + e_b^-$$

where e_{NTTF}^- is the electrons generated from the NTTF after excited by light and e_b^- is the electrons generated from the bias potential ($e_b^- = V_b/R$, where V_b is bias

potential, R is system resistance). The system resistance (R) is fixed, so the e_b^- is proportion to V_b . In other words, the e_b^- can be obtained by testing different bias potentials vs. currents without illumination i.e. the dark current at different bias potentials (shown in Table 2.5). As a result, the e_{NTTF}^- can be calculated by the equation 4, that were 0.07, 0.20, 0.22, 0.34, 0.58 and 0.60 mA for the bias potential at 0.3, 0.5 0.7, 1.0, 1.5 and 2.0 V. In general, the photocurrent should be the same under the same irradiation for the NTTF. However, the photocurrents, in this study, increase with the increasing bias potential. This suggested that the greater the increase in bias potential, which is a kind of driven force, the greater the decrease in recombination of electrons and holes. Meanwhile, applying larger external potential can lead to more electrons to participate in electrochemical oxidation reaction in anode chamber. This result is consistent with the finding of Zhao *et al.* [98] that PCE method can effectively degrade aqueous pollutants by the synergetic effect of electro-oxidation and photocatalysis. This study not only successfully proved the synergetic effect concept in two chamber PCE system, but also quantified the effect of photogenerated currents and holes on photoelectrochemical oxidation for the first time.

Table 2.5. Pseudo-first-order rates of MO degradation (k'_{obs}) under different processes.

Processes	Rate constant	
	$k'_{\text{obs}}, \text{s}^{-1}/\text{cm}^2$	$k'_{\text{obs}}, \text{s}^{-1}$
PEC	4.32×10^{-6}	2.70×10^{-5}
EC	4.32×10^{-7}	2.70×10^{-6}
PC	1.50×10^{-7}	9.40×10^{-7}
P	4.48×10^{-8}	2.80×10^{-7}
Different bias potentials (V)		
0	4.32×10^{-7}	2.70×10^{-6}
0.5	1.31×10^{-6}	8.20×10^{-6}
1.0	1.92×10^{-6}	1.20×10^{-5}
1.5	3.52×10^{-6}	2.20×10^{-5}
2.0	4.32×10^{-6}	2.70×10^{-5}

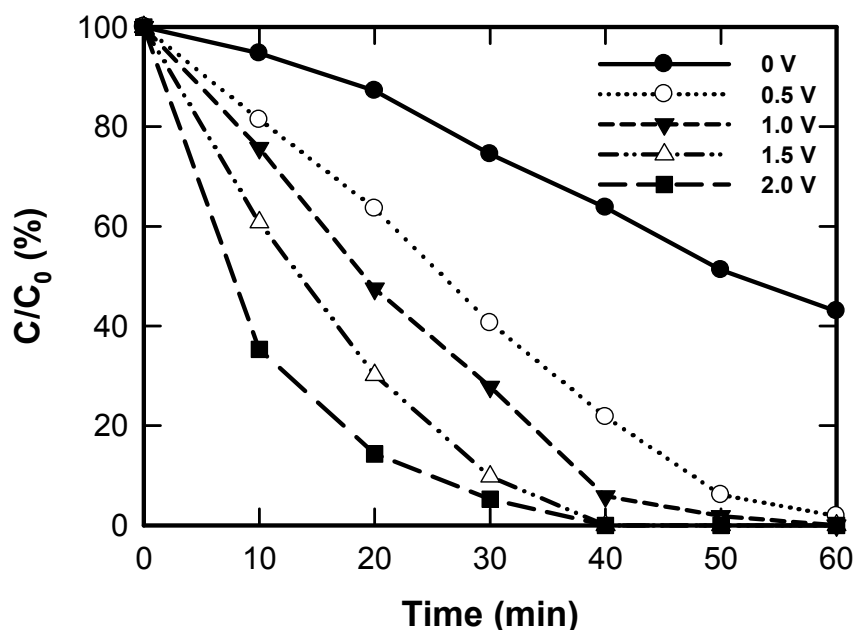
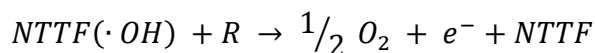
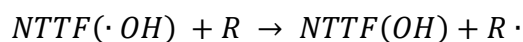


Figure 2.11. Effect of bias potential on PEC degradation of MO. Experimental conditions: anode = NTTF; cathode = copper; initial concentration of MO was 1 ppm; light source = 3.12 mWcm^{-2} (100 W Xe lamp); pH = 6.0 (anode); pH = 6.8 (cathode); electrolyte = 0.1 M NaCl (anode); electrolyte = 0.1 M KHCO_3 (cathode); temperature = 298 K.

2.3.10. Mechanism of MO Degradation

Figure 2.12 presents the schematic diagram of H-type system and the conceptual reaction pathway of the photoelectrochemical oxidation of MO over NTTF. In the anode, the MO molecules first diffused to the border of NTTF surface and then absorbed on it. When a photon has a matched or exceeded bandgap energy, E_g , of the NTTF, electrons are promoted from the valence band into conduction band leaving a hole behind. In general, when there is no suitable scavenger, the photogenerated electrons and holes would recombine rapidly, as mentioned above.

Then, the trapped holes would decrease the oxidation efficiency. In this PEC system, when applying a bias potential, the photogenerated electrons would transfer to the cathode to reduce the recombination. As the current increased, the bias potential increased. Notably, the current, i.e. measured electrons were dominated by photogenerated electrons instead of the electrons from the bias potential. This illustrates that the bias potential is merely worked as a pump which can induce the electrons to escape from the working electrode to the counter electrode. The valence-band hole will react with the H_2O to generate $OH\cdot$ (i.e. surface-bound hydroxyl radical). Most researchers agree that the hydroxyl radical oxidation is the main mechanism for the indirect electrochemical degradation with the existence of organic contaminants. [98, 101, 102]



R represents methyl orange in this study; DP represents degradation products. Thus, the MO in the anode chamber would be oxidized either directly or indirectly by this powerful oxidant. In contrast to single chamber PEC system, reduction reaction rarely occurred in the anode chamber because most electrons were transferred to the cathode (see as Figure 2.12). This phenomenon provides an idea that two-chamber PEC system is favorable for the simultaneous utilization of photogenerated holes and electrons. The studies for photogenerated electrons application in the cathode are under progress in our group. Electrochemical oxidation also makes a contribution to the MO degradation by the generation of oxygen (as eq. 7). Therefore, enhanced oxidation

ability was achieved in this two-chamber PEC system via the combination of electrochemical and photocatalytic reaction.

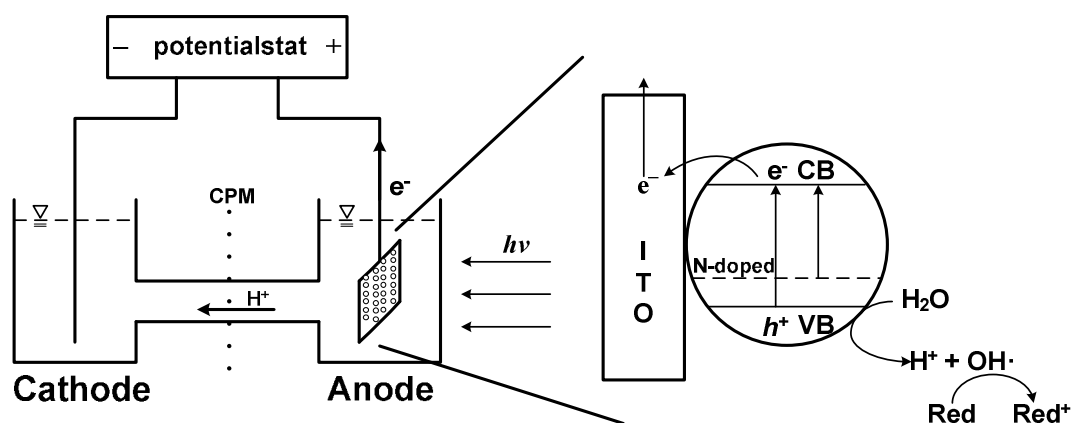


Figure 2.12. Conceptual presentation of the degradation of MO by PEC method over NTTF.

Chapter 3

PHOTOELECTROCHEMICAL REDUCTION OF CO₂ VIA SOLAR CELL SYSTEM

3.1. Introduction

As countries try to develop and grow their economies, their demand for oil increases, as the total available amounts of oil decreases. Although the amount of carbon dioxide is not the most of the emitted gas after inflammation, the emission of carbon dioxide is much higher than other greenhouse gases. According to the National Oceanic and Atmospheric Administration's (NOAA) report in 2011, the carbon dioxide concentration in the atmosphere reached 394.16 ppm. Compare to the report of the Intergovernmental Panel on Climate Change (IPCC) in 2000, it increases 24.16 ppm from 370 ppm. If human are not urged to take measures to reduce carbon dioxide levels, the high concentration of carbon dioxide will cause the global warming. As reported by the U.S. EPA in 2007, the environmental crisis caused by global warming seriously influences human, such as polar ice cap melting and sea level rise to threaten low-lying countries. In addition, droughts, inundation, conflagration, and storms cause human casualty and animal extinction.

Due to the global warming issue which has been concerned recently, in order to decrease the impact caused by global warming, carbon dioxide, which is regarded as one of the key greenhouse gases, Kyoto Protocol have been developed in 1997. The Kyoto mechanism includes emissions trading, the clean development mechanism, and joint implementation. Also, capture technologies have been developed for decades, including electrochemical reduction, photochemical reduction, hydrogenation of carbon dioxide in aqueous solution, biochemical procedures, and thermochemical procedures.

In the development of reducing carbon dioxide to fuels, electrochemical approach has been one of the most popular reduction reactions for the last decades. Compared to storing electricity in batteries or as hydrogen, carbon based fuels are more easily to be used within the existing infrastructures, producing a much higher energy density. And the converting electrical energy to chemical energy process was involved in order to produce this carbon based fuel, thus highlighting the importance of electrochemistry [1]. Based on the general carbon-based energy cycle concepts, water, methanol and methane would be produced by reacting carbon with electrolytic hydrogen. Mikkelsen *et al.* (2009) [2] reviewed that chemical reaction, electrochemical reduction reaction and photocatalytic reduction have been done by many researchers [1, 3-10]. Chemical reduction of carbon dioxide is thermodynamically feasible in the presence of strong reducing agents such as metallic elements (Ti, Fe) and borohydride (BH_4^-). However, it requires the addition of electron-donating chemicals for chemical reduction of carbon dioxide. Photocatalytic, such as TiO_2 , reduction is another way to reduce carbon dioxide. Dey (2007) reviewed chemical reduction of CO_2 using TiO_2 photocatalysts [11]. There are two pathways to yield the hydrocarbons, $\text{CO}_2 \rightarrow \text{HCOOH} \rightarrow \text{HCOH} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_4$ [7, 12, 13] and $\text{CO}_2 \rightarrow \text{CO} \rightarrow \text{C} \cdot \rightarrow \text{CH}_2 \rightarrow \text{CH}_4$ [14-17]. The former mechanism has been anticipated on the basis of the results obtained in condensed media, while the latter has been proposed based on the finding in photocatalytic reduction of high pressure CO_2 using TiO_2 photocatalysts in suspension.

An alternative to photocatalytic reduction of carbon dioxide is electrochemical reduction. Spataru *et al.* (2003) studied reduction of carbon dioxide at RuO_2 -coated diamond electrodes and suggested the formation of formic acid and

methanol [18]. Aydin and Koleli (2004) reported that, under high pressure in methanol, the conversion of carbon dioxide on a polypyrrole electrode can electrochemically produce HCOH, HCOOH, and CH₃OH [19]. Kaneco *et al.* (2006) investigated the electrochemical reduction of carbon dioxide in methanol solution at high pH over copper electrode and reported the production of ethylene [20]. It has been illustrated that the electrode materials and electrolyte used affect the yield of CO₂ reduction products. Some researchers reported that only copper was able to generate a significant amount of hydrocarbon such as methane and ethylene among a total of 16 electrodes studied [10].

However, such process may consume much electricity in order to produce high quality of methane and methanol, leading to consuming “energy” for producing “energy” and non-environmental friendly. A key improvement along the road to solve this tricky problem is photoelectrochemical reaction (PEC). Sun *et al.* (2010) reported that PEC is a perspective technology on water splitting [21]. Zhou *et al.* (2009) successfully applied PEC system to generate hydrogen over carbon-doped TiO₂ photoanode [22]. Although this reduction reaction of carbon dioxide was not popularly used and not fully developed due to the fact that electrons are generated by the photo cells (i.e., photo cells might refer to solar cells or TiO₂ cells, depending on the materials), researchers should still put emphasis on the PEC approach and keep developing and investigating it for further application.

In this chapter, a commercial solar cell was applied in a photoelectrochemical process. This technology is based on solar light as the solar energy source and required no chemicals in the process. The carbon dioxide can be converted into energy-containing organic carbons such as methane, alcohols and

benign organic acids that can be reclaimed using photoelectrochemical approach. In addition, the azo dye can be oxidized simultaneously. For this approach, all electrons are converted from the photons. The converted electrons can be used as reducing agents for carbon dioxide reduction and the anode of the commercial solar cell is able to be used for oxidation reaction for organic compounds, namely, methylene orange.

This study deals mainly to study a sustainable technology for recycling carbon dioxide as energy-containing organic compounds such as alkanes, alcohols, and organic acids and degradation of selected azo dye (methyl orange). The research has the following three specific objectives: (1) to investigate the effect of CO₂ solubility for the photoelectrochemical reduction of carbon dioxide in aqueous solution, (2) to study the kinetic mechanism for the photoelectrochemical reduction of carbon dioxide at copper electrode via solar cell system system, and (3) to study the degradation of selected azo dye (methyl orange) via photoelectrochemical process.

3.2. Materials and Methods

3.2.1. Materials

The electrolyte solution was prepared by dissolving a proper amount of potassium bicarbonate in deionized water prepared in the laboratory using a water-purification system (Mega-Pure System, Model MP-290). Potassium bicarbonate, formaldehyde (purity>37%), methanol, acetonitrile, Sodium hydroxide, sulfuric acid were purchased from Fisher Scientific, USA. Sodium chloride (purity>99%), formic acid (purity>99%), and phosphoric acid (purity>85%) were purchased from ACROS, USA. 2,4-dinitrophenylhydrazine (DNPH), and methyl orange (purity>85%) was purchased from Sigma-Aldrich, USA. A copper wire, curled to be a coil of 0.9 cm in

diameter with length of 35 cm (11 inches) and 1 mm in width, was purchased from Fisher Scientific, USA. The light source, 50 W halogens light, was purchased from Eiko Ltd., USA. The solar cell (4 V, 200 mA, OEM solar panel) was purchased from Sunmaxx Solar, Inc., Ithaca, NY, USA.

3.2.2. Characteristic of Solar Cell

According to information from the manufacturer, SunMaxx Solar, Inc., the conversion efficiency of the OEM solar panel is 13% with voltage (Voc) 4 V, amperage (Isc) 200 mA, wattage 0.8 W; and dimensions 6.5'' (width) $\times$ 3 9/16'' (length), and 1/8 (depth)''.

3.2.3. Photoelectrochemical Reduction of Carbon Dioxide and Degradation of Methyl Orange via Solar Cell

The photoelectrochemical (PEC) activities of the solar were evaluated in terms of carbon dioxide reduction and degradation of methyl orange under halogens light irradiation at ambient temperature. Photoelectrochemical experiments were carried out in a two-electrode system. A copper, curled to be a coil of 0.9 cm in diameter with length of 35 cm (11 inches) and 1 mm in width, was used as the cathode. A single 10 cm long platinum wire was used as the anode. In order to better evaluate the capability of carbon dioxide reduction and degradation of azo dye using PEC system, a two-compartment reactor, self-designed H-type cell, was made to separate the anode and the cathode. These two compartments were connected by a cation membrane. The copper electrode, the cathode, was placed in the cathodic chamber and platinum wire as the anode was in the anodic chamber. The light emitted from a halogens excitation source and irradiated directly onto the solar cell. The light intensity at the surface of the solar cell was about 62 W/cm². The solution volume in

chamber (A) and chamber (B) (see figure 3.1) were 467 and 500 mL, respectively. Electrolyte was provided with 0.1 M of KHCO_3 and 0.1 M of NaCl in chamber (A) and chamber (B), respectively.

Photoelectrochemical reduction of CO_2 was operated in the chamber (A). Before each experiment, carbon dioxide gas was bubbled into 0.1 M potassium bicarbonate (KHCO_3 ; $\text{pH} = 8.3$) solution for 1.5 h at a rate of 12 mL/s until saturated ($\text{pH} = 6.8$). The gas and liquid samples were taken 5 times with the interval of 1 h. The gas and the liquid samples were taken at gas sampling and liquid sampling ports, respectively.

The photoelectrochemical degradation of azo dye, namely, methyl orange was operated at anodic chamber. An amount of 7.27 mole of Methyl orange dissolved in 0.1 M NaCl was used as the electrolyte. Figure 3.1 (a) and figure 3.1 (b) shows the entire setup. In addition, the instruments and experimental conditions for the photoelectrochemical reduction of CO_2 are listed in Table 3.1.

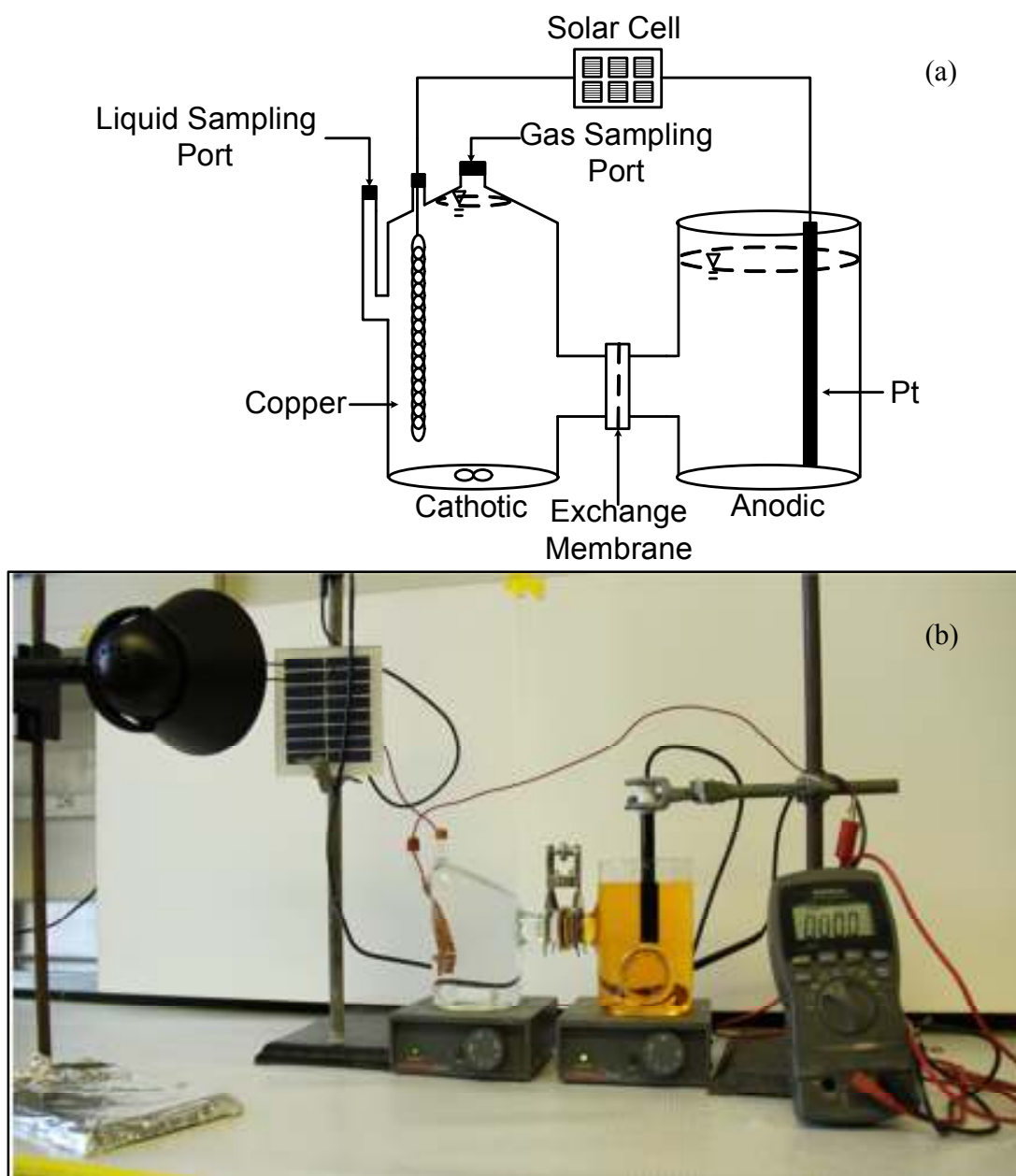


Figure 3.1. (a) Schematic diagram of the photoelectrochemical reduction of CO_2 over a commercial cell (b) photo of experimental setup

Table 3.1. Apparatus and experimental condition of solar cell system

Electrochemical reduction	
Cell	H-type cell
Solar Cell	4 V 200 mA OEM solar panel, Sunmaxx Solar, Inc.
Cathode	Copper Wire (Fisher Scientific, 155451A)
Anode	Pt Wire
Electrolyte	
Catholyte	0.1 M KHCO ₃ in 0%, 20%, and 40% methanol
Anolyte	7.27 mole methyl orange dissolved in 0.1 M of NaCl
Carbon dioxide	99.999% purity
Potential	4 V
Temperature	298.15 K
Product analysis	
<i>Gas products</i>	Gas chromatography
Hydrogen	TCD (HP-5890 series II, Alltech Hayesep D 100/120, He carrier gas)
Methane, methanol	FID (HP-5890 series II, Supelco Supel-Q Plot, He, Air, H ₂ carrier gas)
<i>Liquid products</i>	
Formaldehyde	HPLC with UV detector (HP-Hewlet Packard series 1100, Varian Inertsil 5 μ ODS-2 150 $\times$ 4.6 mm)
Formic acid	IC with conductance detector (Dionex, IonPac AC20 4 $\times$ 250 mm)

3.2.4. Electrode Preparation

Before each experiment, copper wire was pretreated by reversed the polarity of 10 volts in 0.1 M H₂SO₄ every 15 s with a total time of 2 min. The cleaned copper wire electrode was rinsed with distilled water. The platinum electrode was dipped in 1 M H₂SO₄ and connected to 4.5 volt the power supply. A copper wire was used as the counter electrode. The polarity was reversed every 15 s and the platinum

electrode was continuously cleaned for 2 min. After cleaning the platinum electrode, it was rinsed with distilled water.

3.2.5. Analytical Methods

The gas products, hydrogen, was analyzed using a HP gas chromatography system (5890 Series II) with TCD detector (Packing: Alltech Hayesep D 100/120, Tubing: 1/8" Nickel, Length: 20', carrier gas: Helium at 30 mL/min, oven temp.: 35 °C, injection and detector temp.: 120 °C, and sample volume: 100 µL).

Methanol and methane were analyzed using gas chromatography (5890 Series II) with FID detector (Packing: SUPELCO Supel-Q PLOT, fused silica capillary column, 30 m × 0.32 mm). The flow rate of carrier gas (Helium) and fuel gas (air, and hydrogen) were 3, 32, 300 mL/min, respectively. For methanol measurement, oven, injection, and detector temperature were set as 50, 100, and 250 °C, respectively. The injected volume was 2 µL. For methane measurement, oven, injection, and detector temperature were set as 50, 100, 250 °C, respectively. The injected volume was 1 mL.

The liquid sample, formic acid, was analyzed using a Dionex ion chromatograph system with a GP50 pump, ED 40 conductance detector and a AS 40 automated sample. NaOH was used as the mobile phase. The separation part was an IonPac AC20 column (4 × 250 mm). The flow rate of sodium hydroxide effluent was 1 mL/min with a concentration gradient to assure satisfying separation and detection limit. A 200 µL injection loop was used for formic analysis.

Before analyzing formaldehyde, the samples were derivatized using 2,4-dinitrophenylhydrazine (DNPH). The reagent solution was modified according to Lin

[78] by dissolving 5 mg DNPH in 40 mL of solution containing concentrated HCl (12M), water, and acetonitrile in the ratio of 3.5:1:0.52 (v/v/v). The 1.5 mL sample was derivatized by adding 1.5 μ L derivatizing reagent in 2 mL vial. The vial was capped and shaken for 20 seconds, and the reaction was allowed to proceed for 30 min at ambient temperature. Formaldehyde-DNPH was measured by High Performance Liquid Chromatography (HPLC) with a UV detector (hp, Hewlett Packard series 1100). The separation part was a Varian Inertsil 5 μ ODS-2 column (150 $\times$ 4.6 mm). The HPLC system was operated with binary gradients consisting of acetonitrile and acidified water with H₂SO₄ at pH 3.0. The flow rate was 1.0 mL/min. The column was at an ambient temperature. The injection volume was 60 μ L.

Methyl orange samples were measured using UV-Vis (HP 8452A diode array spectrophotometer) over the wavelength of 300 to 600 nm. The absorbance of MO was 450 nm.

3.3. Results and Discussion

3.3.1. Characterization of the Solar Cell

The process of converting sunlight into solar energy requires the absorption of light to excite an electron from the valance band to the conduction band and to move an electron into an external circuit. The electron would be consumed in the external circuit and would then return to the solar cell.

Figure 3.2 shows the current produced by the solar cell at different light intensities. The generated current was 46.7 mA at 123.35 W/m² and increased until it leveled out at approximately 62 mA at 385.82 W/m².

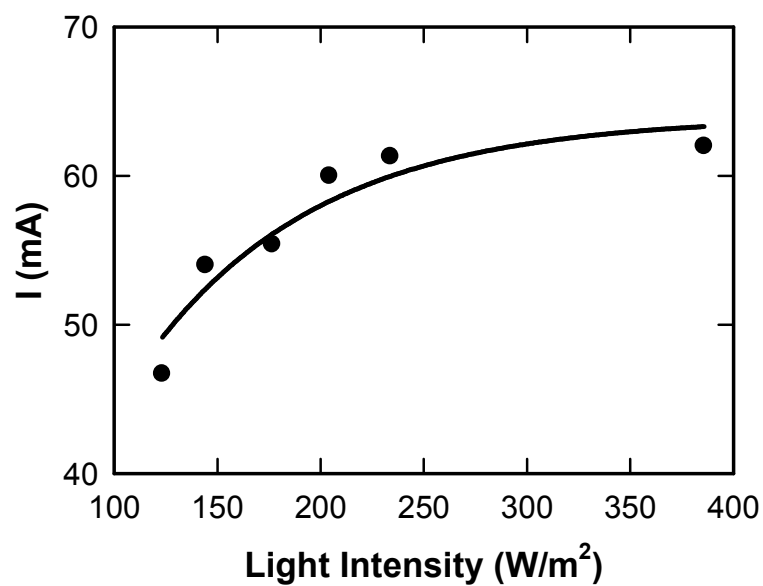


Figure 3.2. Current produced (mA) versus light intensity (W/m²)

3.3.2. Photoelectrochemical Reduction of CO₂ in KHCO₃ Aqueous Solution

Current efficiencies for the photoelectrochemical reduction products of CO₂ on a Cu electrode in KHCO₃ aqueous electrolyte at 298.15 K, as a function of time are illustrated in Table 3.2. Formic acid (HCOOH), formaldehyde (HCOH), methanol (CH₃OH), and methane (CH₄) were detected as CO₂ reduction products. Hydrogen (H₂) was detected as a by-product.

The formation efficiencies of HCOOH, HCOH, and CH₃OH decreased as the reaction time increased. The maximum current efficiencies of HCOOH, HCOH, and CH₃OH were 0.69, 0.38, and 1.13%, respectively, observed in the first hour. However, the formation efficiency of CH₄ increased as reaction time increased. The maximum current efficiency of CH₄ was 1.2%, higher than the maximum current efficiencies of the other products and occurred in the fifth hour. Figure 3.3 shows the measured reaction products from photoelectrochemical reduction of CO₂ in KHCO₃ solution, as a function of reaction. The products HCOOH, HCOH, and CH₃OH were in the liquid phase and CH₄ was in the gas phase. Hydrogen was also detected during the reaction. Naitoh *et al.* reported that the products of CO₂ reduction were produced by the bubbled CO₂ instead of the KHCO₃ solution or methanol. Consequently, the predicted products were converted from the dissolved CO₂ [103]. The observed order of concentrations (μM) was CH₄ > CH₃OH > HCOOH > HCOH. Hori *et al.* (1985) studied the electrochemical reduction of CO₂ at a copper electrode and reported that only HCOOH, CH₄, CO, and H₂ were produced, with current efficiencies of 15.4, 37.1, 1.5, and 32.8%, respectively [6]. Some researchers have suggested that a Cu electrode can reduce CO₂ into formic acid, aldehydes, and alcohols in significant amounts [6, 25, 104, 105]. The current efficiencies of all products in this study were relative lower than those in the literatures. The reason might be that higher current densities were

applied to other systems. For example, the current density in some reports (5 mA cm^{-2}) was much higher than that in this study (0.3 mA cm^{-2}) [6, 25]. As indicated above, the products of this study were HCOOH, HCOH, CH₃OH, and CH₄. Although the current efficiencies of all products in this study were relatively low, significant amounts of HCOOH, HCOH, CH₃OH, and CH₄ were detected in this study.

The formation efficiency of H₂ also increased as reaction time increased. The maximum current efficiency of H₂ was 56.66% at the fifth hour and was much higher than the maximum current efficiency of the products from photoelectrochemical reduction of CO₂. In the photoelectrochemical reduction of CO₂, H₂ formation competes with other CO₂ reduction products. Some researchers found that hydrogen formation current efficiency for electrochemical reduction on Cu was 52% for 50 mmol dm^{-3} KHCO₃ solution and 56% for 500 mmol dm^{-3} CsHCO₃ solution [105, 106].

In this study, the total current efficiency of photoelectrochemical reduction of CO₂ via solar cell did not come close to 100%. The reason is still under investigation.

Table 3.2. Current Efficiency (%) of photoelectrochemical reduction of CO₂ at Cu electrode in KHCO₃ (0.1 M) electrolyte

Time (hr)	HCOOH	HCOH	CH ₃ OH	CH ₄	H ₂	Total
1	0.69	0.38	1.13	0.00	49.32	51.52
2	0.41	0.29	0.83	0.56	50.41	52.49
3	0.30	0.26	0.83	0.76	53.36	55.52
4	0.26	0.20	0.87	0.85	54.11	56.29
5	0.22	0.17	0.84	1.20	54.23	56.66

Catholyte: KHCO₃ (0.1 M), anolyte: NaCl (0.1 M)/5 ppm methyl orange, temperature 298.15 K, potential 4 V, current 3.3 mA

3.3.3. The Effect of CO₂ Solubility on Photoelectrochemical CO₂ Reduction

The effect of CO₂ solubility on its photoelectrochemical reduction was investigated. Figure 3.3 illustrates the effect of varying methanol concentrations in the electrolyte on the yields of reaction products from photoelectrochemical reduction of CO₂. For 0% methanol-based electrolyte, the yield of HCOOH, HCOH, CH₃OH, and CH₄ were 1.55, 0.62, 2.02, and 2.16 μ M, respectively. For 20% methanol-based electrolyte, the yield of HCOOH, HCOH, and CH₄ were 8.76, 0.62 and 3.20 μ M, respectively. For 40% methanol-based electrolyte, the yield of HCOOH, HCOH, and CH₄ were 42.05, 1.88, and 3.94 μ M. The yield of CH₃OH from photoelectrochemical reduction of CO₂ in KHCO₃/20% methanol and in KHCO₃/40% methanol could not be quantified. Thus, the yield of CH₃OH is not discussed in this study. Figure 3.3 also indicates that the amount of HCOOH, HCOH, CH, and CH₄ increased as the methanol concentration of the electrolyte increased. As shown in Table 3.3, current efficiencies of the selected products from photoelectrochemical reduction of CO₂ increased with increasing methanol concentration in the electrolyte. The current efficiency of HCOOH formation increased from 0.22 to 6.88% as the methanol concentration in the electrolyte increased from 0 to 40%. Similar results were observed for HCOH and CH₄ formation. The current efficiency of HCOH and CH₄ formation increased from 0.17 to 0.61% and from 1.20 to 2.58%, respectively.

Table 3.3. Current efficiency (%) of photoelectrochemical reduction of CO₂ at a Cu electrode in KHCO₃/0 to 40% methanol electrolyte

MeOH Conc. (%)	HCOOH	HCOH	CH ₄	H ₂
0	0.22	0.17	1.20	54.23
20	1.34	0.34	1.95	48.54
40	6.88	0.61	2.58	42.91

Catholyte: KHCO₃ (0.1 M), anolyte: NaCl (0.1 M)/5 ppm methyl orange, temperature 298.15 K, potential 4 V, current 3.3, 3.0, and 2.8 mA for KHCO₃/0% methanol, KHCO₃/20% methanol, and KHCO₃/40% methanol, respectively.

H₂ is a product of water electrolysis. Water concentration decreased as the methanol concentration in the electrolyte increased. Figure 3.3 (d) indicates the yield of H₂ decreased as the methanol concentration in the electrolyte increased. The yield of H₂ for 0, 20, and 40% methanol electrolytes was 0.16, 0.14, and 0.11 mM, respectively. Table 3.3 also shows H₂ formation in KHCO₃/20% methanol and KHCO₃/40% methanol electrolytes. In KHCO₃/20% methanol and KHCO₃/40% methanol electrolytes, the current efficiency of hydrogen formation on a Cu electrode at 298.15 K decreased to 48.54 and 42.91%, respectively.

In order to save applied energy on hydrogen evolution instead of being used for CO₂ reduction, to restrain hydrogen formation is important. Some researchers have suggested that the initial concentration of CO₂ affects CO₂ reduction efficiency [75]. A methanol-based electrolyte can not only enhance CO₂ solubility to increase hydrocarbon production, but also suppress hydrogen evolution. Decreasing water concentration might be the reason for this. Kaneco *et al.* found that the current efficiency for hydrogen formation on a Cu electrode at 243 K in CsOH/methanol electrolyte was suppressed to below 23% [54]. For electrochemical reduction of CO₂ on Cu in water, hydrogen formation efficiencies were found to be 56% in 500 mmol

dm^{-3} CsHCO_3 and 52% in 50 mmol dm^{-3} KHCO_3 solutions [105-107]. These results for current efficiencies of hydrogen formation were similar to those of this study. Therefore, it could be proven that a methanol-based electrolyte is one method for suppressing hydrogen formation.

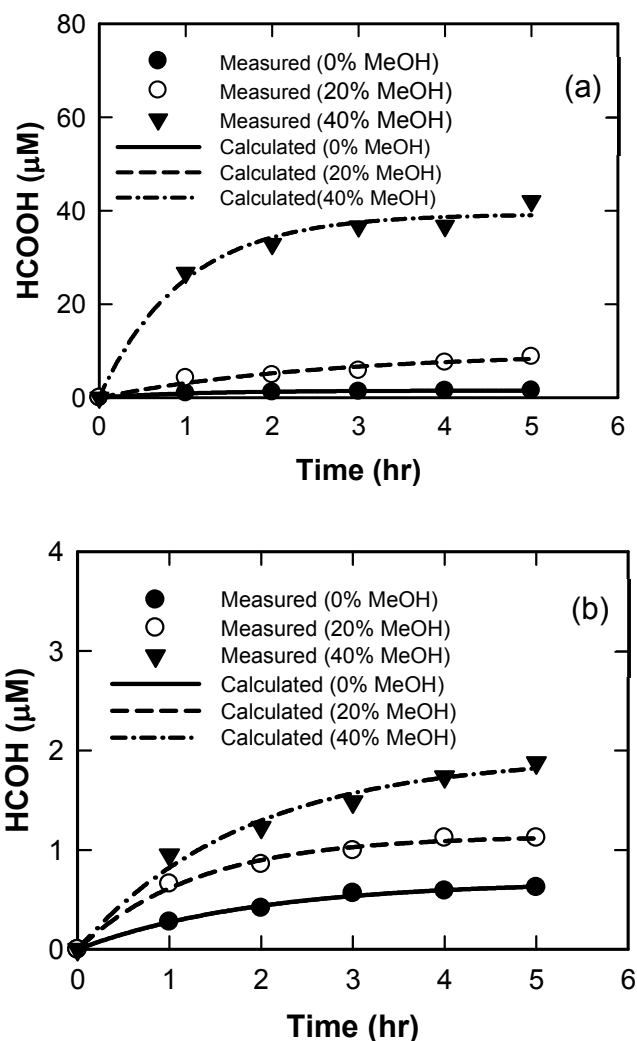


Figure 3.3. The effect of the methanol concentration in catholyte on photoelectrochemical reduction of CO₂ with HCOOH (a), HCOH (b), CH₄ (c), and H₂ (d) concentrations predicted based on differential first-order models. Calculated lines were fitted using Sigma Plot. Experimental conditions: anode = platinum; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO₃/0 to 40% methanol (cathode); pH = 6.0 (anode); pH = 6.8 (cathode); temperature = 298.15 K; light source = halogens light (E 192412, Eiko Ltd., USA; 50 W).

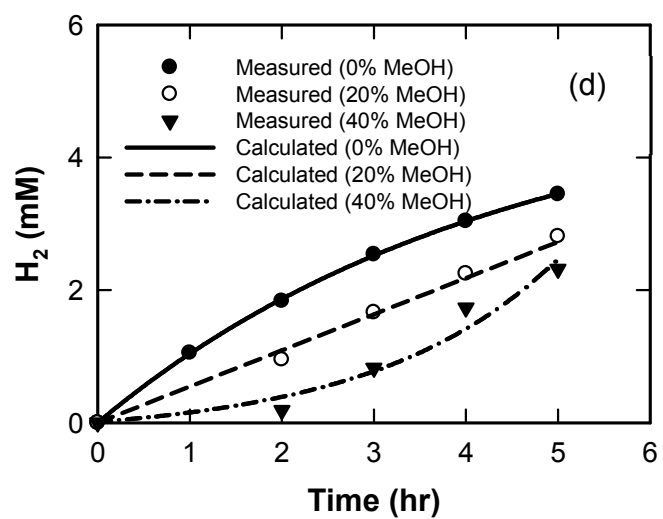
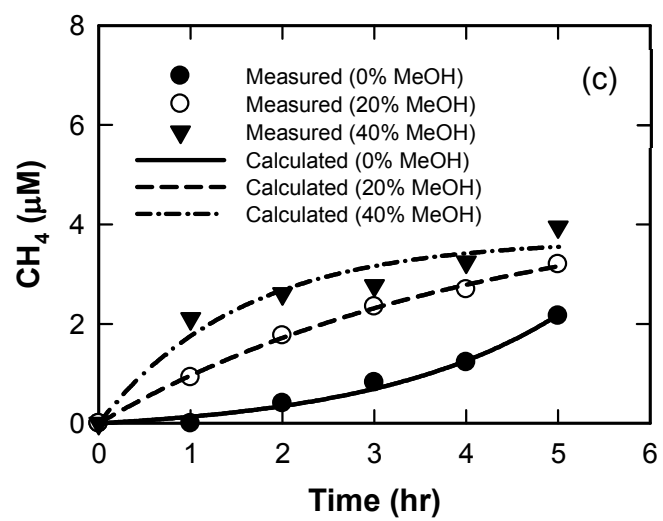
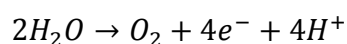


Figure 3.3. continued

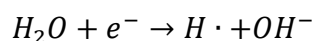
3.3.4. Reaction Mechanism

All energy was provided by the solar cell. Electro-reduction reaction and electro-oxidation reactions occurred simultaneously at the cathode and the anode, respectively. The mechanism for photoelectrochemical reduction of CO₂ in a KHCO₃ aqueous solution with a copper electrode was investigated. Kaneco *et al.* reported that when electrolysis was conducted under nitrogen atmosphere, only hydrogen gas would be produced [20, 43, 54]. Also, Teeter and Van Rysselberghe [108] established that only dissolved CO₂ molecules reacted during the reduction instead of bicarbonate HCO₃⁻ or carbonate CO₃²⁻ ions from solution. CO₂ is the only reducible species. Consequently, all products were produced by photoelectrochemical reduction of the dissolved CO₂. On the basis of these experimental results and literature reports [76, 109, 110], a possible pathway of CO₂ reduction for HCOOH, HCOH, CH₃OH, and CH₄ on a Cu electrode can be investigated. A possible mechanism for hydrocarbon formation at the Cu electrode may involve the following steps: Once the solar cell was excited, holes and electrons were generated. a potential was also applied by the solar. As the potential was applied, the water at the anode is first oxidized into oxygen (O₂), proton (H⁺), and electrons (e⁻):

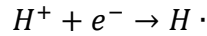


Notably, the oxygen electrolyzed from water is advantageous for pollutant oxidation.

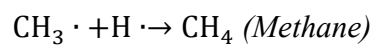
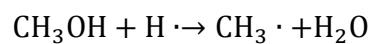
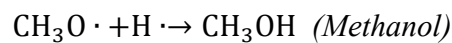
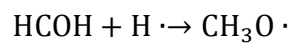
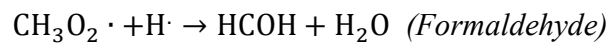
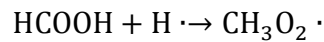
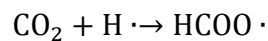
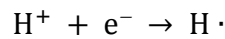
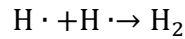
The protons would pass from anodic chamber to cathodic chamber through the cation exchange membrane, separating the two chambers. The photon-generated electrons react with water adsorbed on the copper electrode, resulting in the production of hydrogen radicals (H[·]) and hydroxyl ions (OH⁻):



The protons passing from the anodic chamber also lead to formation of hydrogen radicals:



The strong reductant, hydrogen radicals, would then rapidly combine to produce hydrogen which is a useful energy source or would contribute to the carbon dioxide reduction reaction in each step. Once the carbon dioxide molecules react with the hydrogen radicals, the hydrocarbons, formic acid, formaldehyde, methanol, and methane, are produced in a series reaction [12, 13]. The possible mechanism at cathode is listed below:



Hydrogen radicals are required for hydrocarbon formation in each step. Thus, the hydrogen radical might be an important reduction agent for CO₂ reduction. A conceptual presentation of reduction of CO₂ in a solar cell system is shown in the figure 3.4.

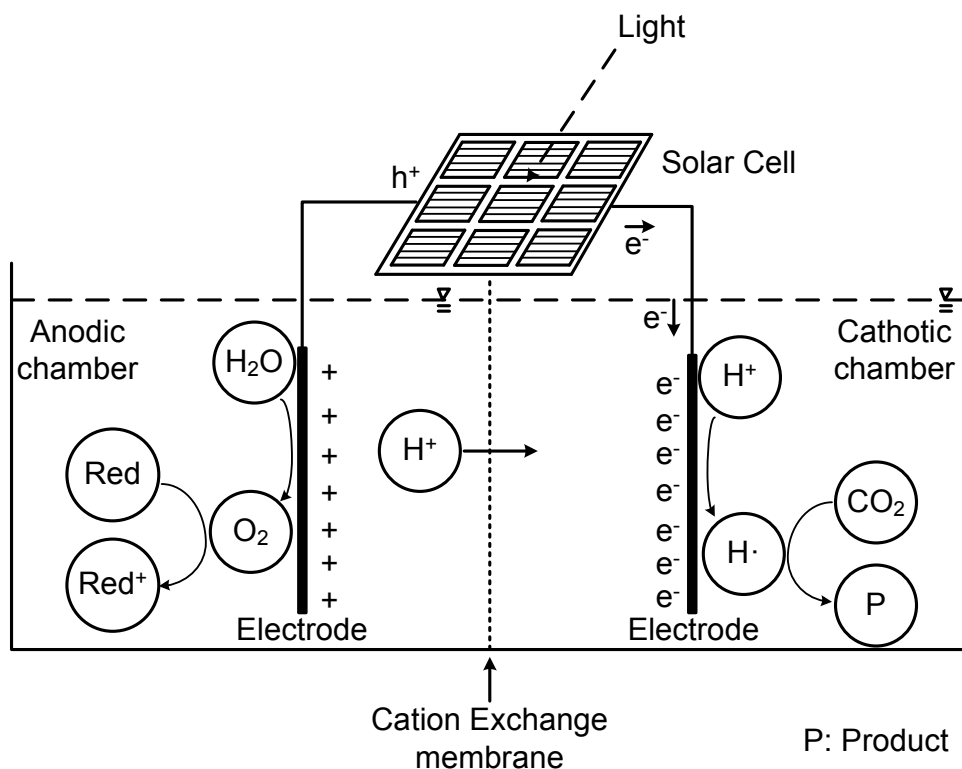
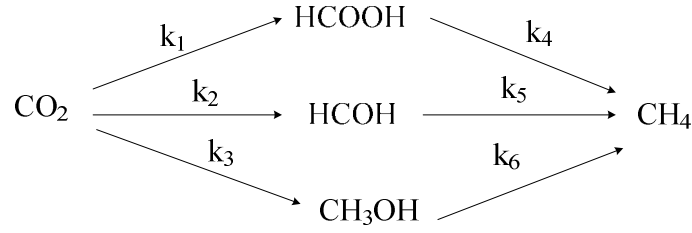


Figure 3.4. Conceptual presentation of CO₂ reduction and MO degradation by the PEC method using a solar cell.

3.3.5. Kinetic Study of PEC Reduction of CO₂

The reaction pathway for photoelectrochemical reduction of CO₂ in 0.1 M KHCO₃ solution at a copper electrode was investigated. In this study, first-order kinetics was assumed for photoelectrochemical reduction to hydrocarbons through parallel and series reactions:



According to the assumption, the CO_2 reduction process can be written as a series of first-order reactions,

$$\frac{d[\text{CO}_2]}{dt} = -(k_1 + k_2 + k_3)[\text{CO}_2] \quad (3.1)$$

Set $k_1 + k_2 + k_3 = k_7$

$$\frac{d[\text{HCOOH}]}{dt} = k_1[\text{CO}_2] - k_4[\text{HCOOH}] \quad (3.2)$$

$$\frac{d[\text{HCOH}]}{dt} = k_2[\text{CO}_2] - k_5[\text{HCOH}] \quad (3.3)$$

$$\frac{d[\text{CH}_3\text{OH}]}{dt} = k_3[\text{CO}_2] - k_6[\text{CH}_3\text{OH}] \quad (3.4)$$

$$\frac{d[\text{CH}_4]}{dt} = k_4[\text{HCOOH}] + k_5[\text{HCOH}] + k_6[\text{CH}_3\text{OH}] \quad (3.5)$$

Where t is reaction time and k_1 , k_2 , and k_3 are the reaction rate constants of CO_2 , k_4 , k_5 , and k_6 are the reaction rate constants of HCOOH , HCOH , and CH_3OH , respectively.

Because equations (3.1) to (3.5) are sequential, they can be solved as follows:

$$[\text{CO}_2] = [\text{CO}_2]_0 e^{-k_7 t} \quad (3.6)$$

$$[\text{HCOOH}] = \frac{k_1[\text{CO}_2]_0}{k_4 - k_7} (e^{-k_7 t} - e^{-k_4 t}) \quad (3.7)$$

$$[\text{HCOH}] = \frac{k_2[\text{CO}_2]_0}{k_5 - k_7} (e^{-k_7 t} - e^{-k_5 t}) \quad (3.8)$$

$$[\text{CH}_3\text{OH}] = \frac{k_3[\text{CO}_2]_0}{k_6 - k_7} (e^{-k_7 t} - e^{-k_6 t}) \quad (3.9)$$

$$[CH_4] = [CO_2] - [CO_2]_0 e^{-k_7 t} - \frac{k_1[CO_2]_0}{k_4 - k_7} (e^{-k_7 t} - e^{-k_4 t}) - \frac{k_2[CO_2]_0}{k_5 - k_7} (e^{-k_7 t} - e^{-k_5 t}) - \frac{k_3[CO_2]_0}{k_6 - k_7} (e^{-k_7 t} - e^{-k_6 t}) \quad (3.10)$$

The effect of irradiation time on the formation of products of photoelectrochemical reduction of CO₂ was investigate over a period of 0 to 5 hours at copper electrode in a solar cell system. The results of data processing by Residual Sum of Squares (SSR), calculated using an Excel solver, are listed in table 3.4. The best combination of reaction constants was calculated. The reaction rate constants of k₁, k₂, and k₃, are 4.43×10^{-9} , 1.39×10^{-9} , $3.09 \times 10^{-9} \text{ s}^{-1}/\text{cm}^2$, respectively, The reaction rate constants of k₄ k₅, and k₆ are 1.87×10^{-6} , 5.55×10^{-7} , and $5.43 \times 10^{-9} \text{ s}^{-1}/\text{cm}^2$, respectively. Notably, the rate constant of carbon dioxide was much smaller than that of the reaction rate constants of all other products. The reason might that the initial carbon dioxide concentration, 0.13 M, was much higher than that of the other products. Figure 3.5 is a comparison of experimental and simulated data for photoelectrochemical reduction of CO₂. Only CH₃OH and CH₄ formation corresponded with the simulation curve from the model listed above.

The coefficient of index of agreement (IOA) can determine the performance of the model simulation [95, 96],

$$d_1 = 1 - \frac{\sum_{i=1}^N (|P_i - O_i|)}{\sum_{i=1}^N (|P_i - \bar{O}| + |O_i - \bar{O}|)} \quad (3.11)$$

where d_1 is the value of IOA; P_i and O_i are the predicted and measured values, respectively, with a sample size N ; and $\bar{O}$ is the average of all measured data. Table 3.4 compares the statistical data for measured and simulated HCOOH, HCOH, CH₃OH and CH₄. Agreement between prediction and measurement is regarded as good when IOA exceeds 0.5 [96].

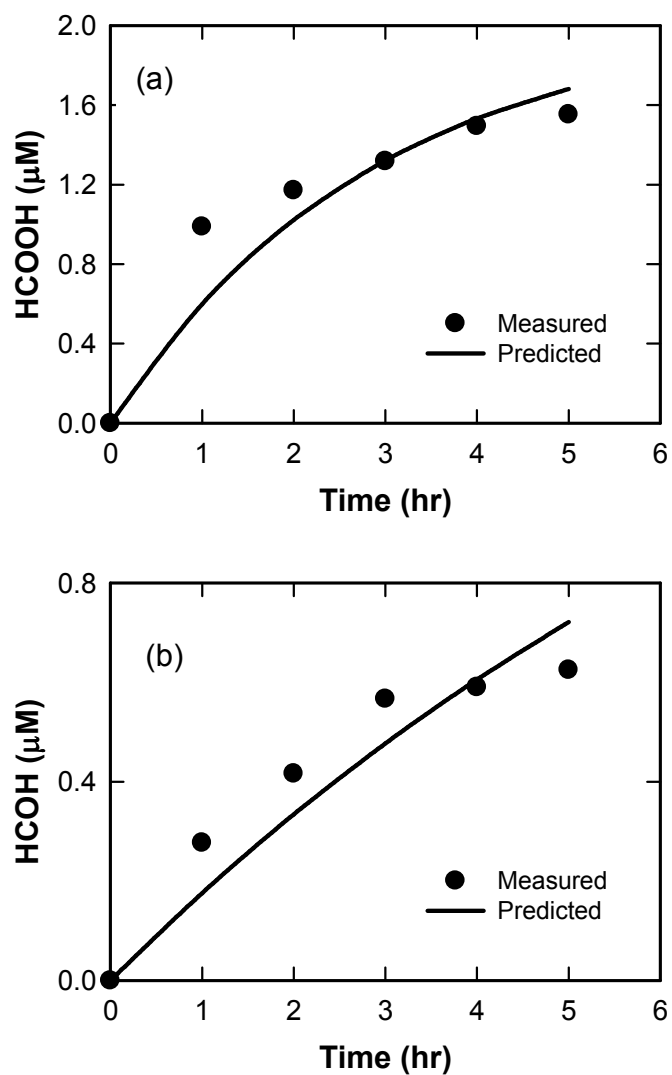


Figure 3.5. Comparison of experimental data with predicted (a) HCOOH, (b) HCOH, (c) CH₃OH, and (d) CH₄ concentrations based on differential first-order models. Predicted data were calculated using equation 3.7 to 3.10. Experimental conditions: anode = platinum; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO₃ (cathode); pH = 6.0 (anode); pH = 6.8 (cathode); temperature = 298.15 K; light source = halogens light (E 192412, Eiko Ltd., USA; 50 W).

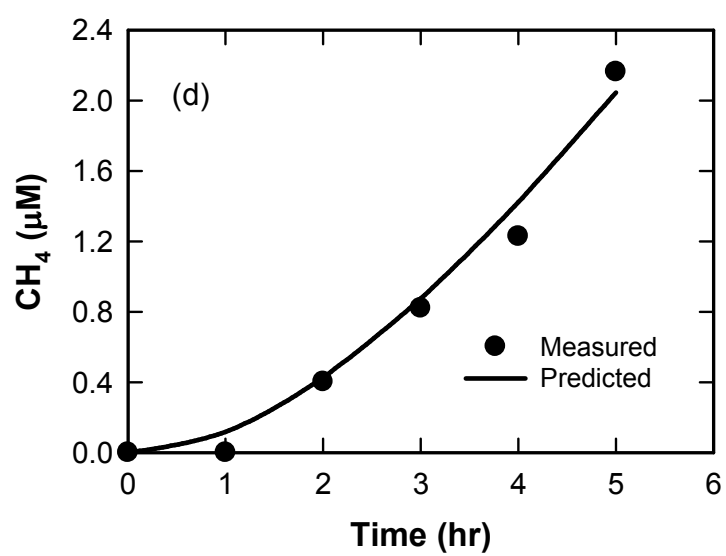
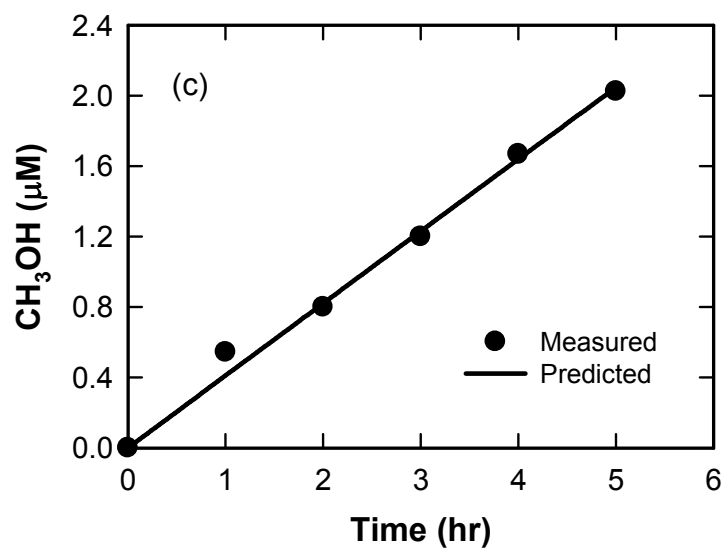


Figure 3.5. continued

Table 3.4. The rate constant (k) of photoelectrochemical reduction of CO₂ at Cu electrode in KHCO₃ (0.1 M) electrolyte

	Kinetic rate constant		IOA
	k, s ⁻¹ /cm ²	k, s ⁻¹	
k ₁	4.43 × 10 ⁻⁹	2.72 × 10 ⁻⁷	
k ₂	1.39 × 10 ⁻⁹	7.12 × 10 ⁻⁸	
k ₃	3.09 × 10 ⁻⁹	1.58 × 10 ⁻⁷	0.87
k ₄	1.87 × 10 ⁻⁶	9.55 × 10 ⁻⁵	0.84
k ₅	5.55 × 10 ⁻⁷	2.84 × 10 ⁻⁵	0.97
k ₆	5.43 × 10 ⁻⁹	2.78 × 10 ⁻⁷	0.93

Catholyte: KHCO₃ (0.1 M), anolyte: NaCl (0.1 M), temperature 298.15 K, potential 4 V, current 3.3 mA

The other pathway was assumed as a series reaction:



According to the assumption, the CO₂ reduction process can be written as a series of first-order reactions,

$$\frac{d[CO_2]}{dt} = -k_1[CO_2] \quad (3.11)$$

$$\frac{d[HCOOH]}{dt} = k_1[CO_2] - k_2[HCOOH] \quad (3.12)$$

$$\frac{d[HCOH]}{dt} = k_2[HCOOH] - k_3[HCOH] \quad (3.13)$$

$$\frac{d[CH_3OH]}{dt} = k_3[HCOH] - k_4[CH_3OH] \quad (3.14)$$

$$\frac{d[CH_4]}{dt} = k_4[CH_3OH] \quad (3.15)$$

Where t is reaction time and k_1 , k_2 , k_3 , and k_4 are the reaction rate constants of CO₂, HCOOH, HCOH, and CH₃OH, respectively.

Because equations (3.11) to (3.15) are sequential, they can be solved as follows:

$$[CO_2] = [CO_2]_0 e^{-k_1 t} \quad (3.16)$$

$$[HCOOH] = [HCOOH]_0 e^{-k_2 t} + \frac{k_1 [CO_2]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (3.17)$$

$$[HCOH] = [HCOH]_0 e^{-k_3 t} + \frac{k_2 [HCOOH]_0}{k_3 - k_2} (e^{-k_2 t} - e^{-k_3 t}) + \frac{k_2 k_1 [CO_2]_0}{k_3 - k_2} \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} - \frac{e^{-k_1 t} - e^{-k_3 t}}{k_3 - k_1} \right) \quad (3.18)$$

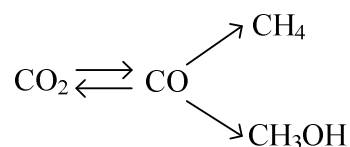
$$[CH_3OH] = [CH_3OH]_0 e^{-k_4 t} + \frac{k_3 [HCOH]_0}{k_4 - k_3} (e^{-k_3 t} - e^{-k_4 t}) + \frac{k_3 k_2 [HCOOH]_0}{k_3 - k_2} \left(\frac{e^{-k_2 t} - e^{-k_4 t}}{k_4 - k_2} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right) + \frac{k_3 k_2 k_1 [CO_2]_0}{(k_2 - k_1)(k_3 - k_1)} \left(\frac{e^{-k_1 t} - e^{-k_4 t}}{k_4 - k_1} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right) - \frac{k_3 k_2 k_1 [CO_2]_0}{(k_2 - k_1)(k_3 - k_2)} \left(\frac{e^{-k_2 t} - e^{-k_4 t}}{k_4 - k_2} - \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_3} \right) \quad (3.19)$$

$$[CH_4] = k_1 k_2 k_3 [CO_2]_0 \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{(k_4 - k_3)(k_3 - k_2)(k_2 - k_1)} - \frac{e^{-k_1 t} - e^{-k_3 t}}{(k_4 - k_3)(k_3 - k_2)(k_3 - k_1)} - \frac{e^{-k_1 t} - e^{-k_2 t}}{(k_4 - k_3)(k_4 - k_2)(k_2 - k_1)} + \frac{e^{-k_1 t} - e^{-k_4 t}}{(k_4 - k_3)(k_4 - k_2)(k_4 - k_1)} + \frac{e^{-k_1 t} - e^{-k_2 t}}{k_3(k_3 - k_2)(k_2 - k_1)} - \frac{e^{-k_1 t} - e^{-k_3 t}}{k_3(k_3 - k_2)(k_3 - k_1)} + \frac{e^{-k_1 t} - e^{-k_2 t}}{k_3 k_2(k_2 - k_1)} + \frac{e^{-k_1 t} - 1}{k_3 k_2 k_1} \right) \quad (3.20)$$

The effect of irradiation time on the formation of products from photoelectrochemical reduction of CO_2 was investigated over a period of 0 to 5 hours at a copper electrode in a solar cell system. The results of data processing by SSR, calculated using an Excel solver, are listed in table 3.5. The best combination of reaction constants was calculated. The reaction rate constant of k_1 , k_2 , k_3 , and k_4 are 9.55×10^{-9} , 4.53×10^{-6} , 1.13×10^{-5} , and $2.52 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$, respectively. Notably,

the rate constant of carbon dioxide was much smaller than those of all other products. The reason might be that the initial concentration carbon dioxide, 0.13 M, was much higher than that of the other products. Figure 3.6 is a comparison of experimental versus simulated data for photoelectrochemical reduction of CO₂. All of the formation products formation corresponded with the simulation curves according to the model listed above.

The IOA values of this assumption were calculated using equation (3.11). Table 3.5 also summarizes statistical data for the comparison of measured and simulated HCOOH, HCOH, CH₃OH and CH₄. Figure 3.6 indicates that the assumed model in this study is suitable for HCOOH, HCOH, CH₃OH, and CH₄ formation. Koci *et al.* [76] studied the kinetics of photocatalytic reduction of CO₂ over TiO₂ using a Langmuira-Hinshelwood (L-H) type kinetic equation and assumed that the reaction mechanisms of CO₂ reduction were



The Koci's group reported that the reaction rate constants were $5.01 \times 10^{-4} \text{ s}^{-1}$ for CH₄ formation and $5.02 \times 10^{-5} \text{ s}^{-1}$ for CH₃OH production [76]. Lo *et al.* investigated the photoreduction of carbon dioxide with H₂ and H₂O over TiO₂ and ZrO₂ in a circulated photocatalytic reactor [75]. Lo's group used a L-H kinetic equation and found that the reaction rate constants of carbon dioxide were 3.5×10^{-6} and $2.08 \times 10^{-6} \text{ s}^{-1}$ at different experimental condition [75]. The kinetic reaction rate constant of CH₄ in this study was slightly lower than the kinetic reaction of rate constant found in literature. and the literature, but the kinetic rate constant of CH₃OH was higher. The initial

concentration (99.999%) of CO₂ in this study was much higher than that in the literature (5%). Therefore, the reaction rate constant of CO₂ in this study ($4.89 \times 10^{-7} \text{ s}^{-1}$) was lower than that in the literature ($2.08 \times 10^{-6} \text{ s}^{-1}$). Although the kinetic reaction rate constants of CO₂ and CH₄ were lower than those reported in the literature, the kinetic reaction rate constants of HCOOH and HCOH can be successfully estimated in both assumptions in this study. It should be noted that even though all IOA values exceeded 0.5, the IOA values for series reactions were higher than those for parallel reactions (as shown in table 3.4 and table 3.5). Therefore, a series reaction might be a more reasonable pathway. Also, it can be concluded that PEC reduction of CO₂ via solar cell cannot only reduce CO₂ into hydrocarbon using sustainable energy, but also can produce more types of products with significant kinetic reaction rate constants.

Table 3.5. The rate constant (k) of photoelectrochemical reduction of CO₂ at Cu electrode in KHCO₃ (0.1 M) electrolyte

	Kinetic rate constant		IOA
	k, s ⁻¹ /cm ²	k, s ⁻¹	
k ₁	9.55×10^{-9}	4.89×10^{-7}	0.927
k ₂	4.53×10^{-6}	2.32×10^{-4}	0.929
k ₃	1.13×10^{-5}	5.79×10^{-4}	0.923
k ₄	2.52×10^{-6}	1.29×10^{-4}	0.932

Catholyte: KHCO₃ (0.1 M), anolyte: NaCl (0.1 M), temperature 298.15 K, potential 4 V, current 3.3 mA

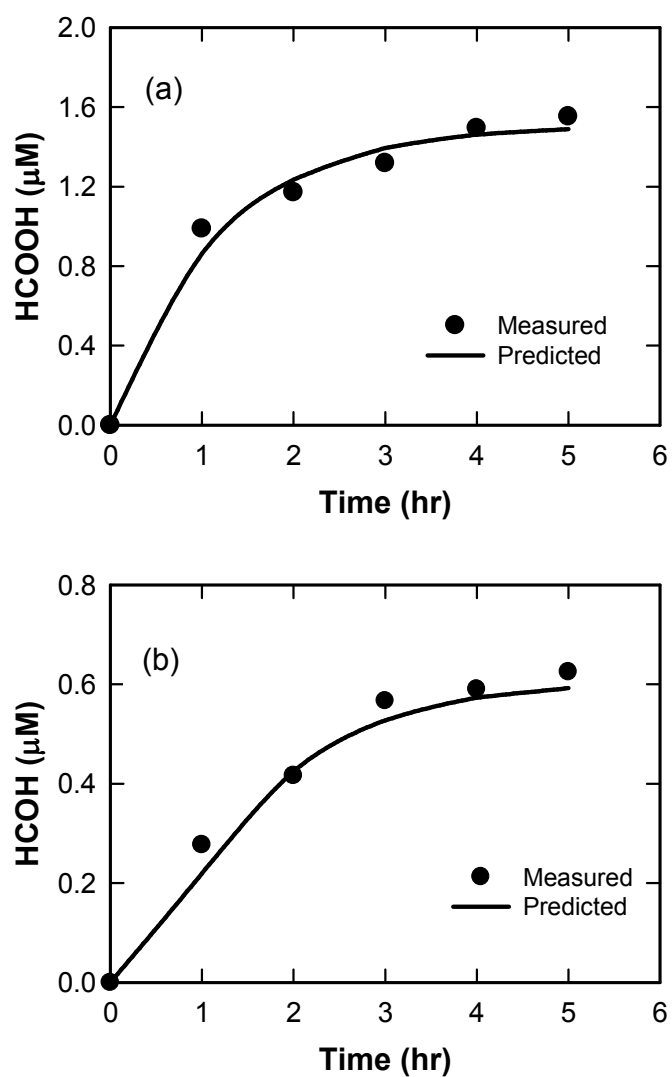


Figure 3.6. Comparison of experimental data with predicted (a) HCOOH, (b) HCOH, (c) CH₃OH, and (d) CH₄ concentrations based on differential first-order models. Predicted data were calculated using equations 3.17 to 3.20. Experimental conditions: anode = platinum; cathode = copper; electrolyte = 0.1M NaCl (anode); electrolyte = 0.1 MKHCO₃ (cathode); pH = 6.0 (anode); pH = 6.8 (cathode); temperature = 298.15 K; light source = halogens light (E 192412, Eiko Ltd., USA; 50 W).

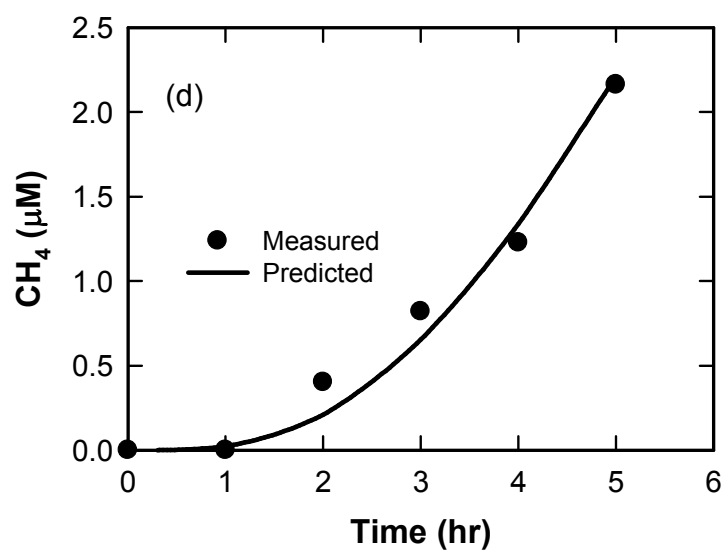
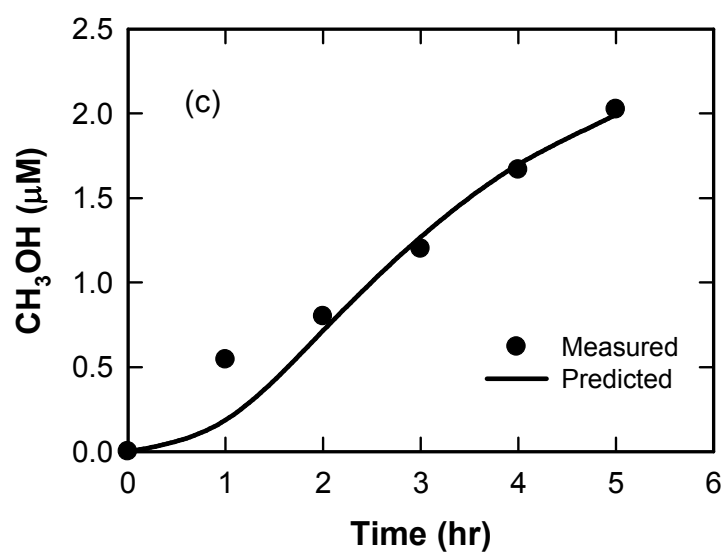


Figure 3.6. continued

3.3.6. Photoelectrochemical Oxidation of Azo Dye (Methyl Orange)

Methyl orange (MO) degradation was performed to evaluate degradation efficiency during photoelectrochemical reduction of CO₂. As shown in figure 3.7, the degradation rate of MO increases as a function of reaction time. It is clearly illustrated that higher currents applied to the system were more effective for degrading MO. In all experimental conditions, methyl orange removal started at the beginning of the reaction. However, the complete removal of 5 ppm MO was observed at the third hour with an applied current of 3.3 mA while 99 and 88% MO removal was achieved at the third hour for 3.0 and 2.8 mA, respectively. A pseudo-first-order kinetic was applied in the photoelectrochemical oxidation of the selected azo dye, MO, using

$$\ln \left(\frac{[MO]_t}{[MO]_0} \right) = kt \quad (3.35)$$

where k is the kinetic constant and t is reaction time. $[MO]_0$ represents the initial concentration of methyl orange. The reaction rate constants were $9.33 \times 10^{-5} \text{ s}^{-1}/\text{cm}^2$ for an applied current of 3.3 mA, $8.31 \times 10^{-5} \text{ s}^{-1}/\text{cm}^2$ for 3.0 mA, $7.13 \times 10^{-4} \text{ s}^{-1}/\text{cm}^2$ for 2.8 mA, and $1.54 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$ for dark condition. Dark condition means that the degradation of MO was performed in a PEC system without irradiating on the solar cell. In the solar system, electrochemical, photochemical, and photoelectrochemical approaches are the same. Thus, the reaction rate constants of EC, PC, and PEC are equal. The value of kinetic rate constant of MO in the dark condition was 100 time less than those in other conditions. The main reason is that the current in the dark condition was 3 μA which is 1000 time less than those in other condition. Zhao *et al.* (2007) studied that photoelectrocatalytic degradation of triazine-containing azo dyes at $\gamma\text{-Bi}_2\text{MoO}_6$ film electrode under visible light irradiation ($\lambda > 420 \text{ nm}$) and reported that the pseudo-first-order kinetic reaction rate constants of azo dye were $1.63 \times 10^{-4} \text{ s}^{-1}$

for the photoelectrochemical process, $4.61 \times 10^{-5} \text{ s}^{-1}$ for the electrochemical approach, and $1.17 \times 10^{-5} \text{ s}^{-1}$ for photocatalytic process, respectively [99]. Comparing the PEC approach in this study and the results of Zhao's group, it is found that the kinetic constant in this study is slightly higher. Notably, a bias potential was applied in the PEC system in Zhao's study; however, in this study, all energy was generated using solar cell. Thus, the approach in this study is a sustainable technology for pollutant oxidation.

A conceptual presentation of MO oxidation over a PEC system is shown in figure 3.4. Once the solar cell was irradiated, water was oxidized to form O_2 , protons, and electrons ($2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} + 4\text{e}^-$). The formation of oxygen is an advantageous for pollutant oxidation. The selected azo dye, methyl orange, was oxidized by the produced O_2 . Notably, the different applied currents, even though the solar cell was irradiated by the same light intensity, might be caused by methanol concentration at cathodic chamber. Higher methanol concentrations in the cathodic chamber caused higher resistance in the system.

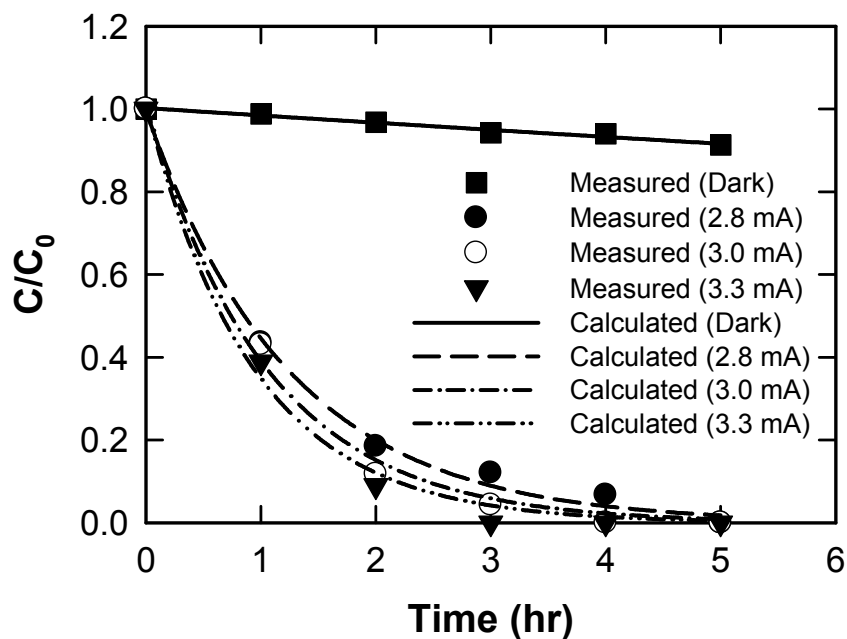


Figure 3.7. Effect of current applied in cathode on PEC degradation of MO. Trends lines were the curve fitting using Sigma Plot. Experimental conditions: anode = platinum; cathode = copper; initial concentration of MO was 5 ppm; light source = Halogens light (E 192412, Eiko Ltd., USA; 50 W); pH = 6.0 (anode); pH = 6.8 (cathode); electrolyte = 0.1 M NaCl (anode); electrolyte = 0.1 M KHCO_3 (cathode); temperature = 298.15 K

Chapter 4

SUMMARY

4.1. Significant Finding

The photoelectrochemical reduction of CO_2 into hydrocarbon using a Cu electrode in different concentrations of methanol-based catholyte at 298.15 K, and degradation of methyl orange at ambient temperature and pressure were investigated. Two different systems, a solar cell and a N-doped TiO_2 thin film system were used in this study. Formic acid, formaldehyde, methanol, and methane were produced by the photoelectrochemical reduction of CO_2 while hydrogen was formed by water electrolysis in both systems. The maximum current efficiencies of the products in the solar cell system were 0.69% for HCOOH , 0.38% for HCOH , 1.13% for CH_3OH , and 1.2% for CH_4 formation. The maximum current efficiency of hydrogen was 56.66%. For the N-doped TiO_2 thin film system, the current efficiencies at the fifth hour for HCOOH , HCOH , CH_3OH , and CH_4 were 2.6, 0.39, 3.26, and 7.83%, respectively. However, the maximum current efficiency of hydrogen was only 50.34%.

Increasing the methanol concentration in the catholyte not only increased the solubility of CO_2 , but also decreased the water concentration as a means of suppressing hydrogen formation. The current efficiency of hydrogen decreased from 54.32% to 42.91% in the solar cell system as the methanol concentration increased from 0% to 40%. This phenomenon was also seen in the N-doped TiO_2 system thin film system. In addition, the current efficiencies of all products from photoelectrochemical reduction of CO_2 increased as methanol concentration increased

from 0% to 40%. The reaction rate constants for HCOOH, HCOH, CH₃OH, and CH₄ were predicted by differential first-order models and were found to be 9.55×10^{-9} , 4.53×10^{-6} , 1.13×10^{-5} , and $2.52 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$, respectively, for the solar cell system and 1.30×10^{-8} , 4.26×10^{-6} , 1.68×10^{-5} and $4.43 \times 10^{-6} \text{ s}^{-1}/\text{cm}^2$ for the N-doped TiO₂ system.

On the basis of the high IOA values, a differential kinetic model can be successfully applied to simulate the photoelectrochemical reduction of CO₂ in both systems. Furthermore, methyl orange can be degraded simultaneously with the degradation rate of 9.33×10^{-5} , 8.31×10^{-5} , and $7.13 \times 10^{-5} \text{ s}^{-1}/\text{cm}^2$ for applied current of 3.3, 3.0, and 2.8 mA, respectively. The electrochemical, photocatalytic, and photoelectrochemical degradation of methyl orange was also investigated. The results illustrated that the photoelectrochemical method can successfully separate the electrons and holes.

This research may contribute to the application of sustainable energy from solar cells not only reduce CO₂ in cathodic chamber, but also to oxidize azo dye in the anodic chamber simultaneously. The effect of CO₂ solubility was also investigated. This study also proved the reaction mechanism for photoelectrochemical reduction of CO₂ in KHCO₃ aqueous solution at a Cu electrode at ambient temperature and pressure using a solar cell and a N-doped TiO₂ thin film with the differential first-order models. Although the photoelectrochemical reduction rates and the yields of all products were relatively low, the investigation has value for future study.

4.2. Future Work

Based on the results in this study, the current efficiencies of all products and yields are low. The products we found were only formic acid, formaldehyde,

methanol, and methane. However, some high molecular weight hydrocarbon might also be formed during the reaction. Furthermore, to increase the current efficiencies and the yields of hydrocarbon will be out goals in the future.

The CO_2 solubility in the electrolyte affects the current efficiency of hydrocarbon production. In order to increase the CO_2 solubility in the electrolyte, one can increase the system pressure and decrease the system temperature. In addition, hydrogen formation suppresses CO_2 reduction. Decrease in hydrogen formation is important in this study. The effect of type of cathode on performance of the PEC system might also need to be investigated.

In our assumption, the CO_2 reduction is a series reaction and the products include formic acid, formaldehyde, methanol, and methane. However, we did not investigate that the products were produced from which hydrocarbon. Also, some other hydrocarbons, such as ethylene and ethane, might also be formed at low concentration. Using GC-MS to measure the hydrocarbons can not only analyze the source of carbon, but also increase the detection limit.

Finally, azo dye can be degraded with different reaction rate constant under different experimental conditions. Therefore, the effect of anode types, the pH value of azo dye, and the electrolytes in the anodic chamber might also need to be investigated.

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