

DESIGN, CONSTRUCTION AND TESTING OF VARIOUS REACTOR GEOMETRIES
FOR GAS-PHASE PHOTOCATALYTIC CARBON DIOXIDE REDUCTION

by

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ABSTRACT

DESIGN, CONSTRUCTION AND TESTING OF VARIOUS REACTOR GEOMETRIES FOR GAS-PHASE PHOTOCATALYTIC CARBON DIOXIDE REDUCTION

This thesis proposes a comprehensive preliminary design of a gas-phase photocatalytic carbon dioxide reduction system with water. The aim was to design, construct and operate a reaction system using titania-based photocatalytic materials and various sources of light. To accomplish this, the lab-scale process system was constructed from scratch, which was followed by calibration of the equipment, synthesis of the photocatalyst material, and initial operation of the process as a whole under varying operating conditions. The main operational variables were the type of light source, the weight of photocatalyst, the inlet gas flowrates and the water heating of the water bubbler, which was used to generate moisture and transport it with CO₂ into the system. The reactions were carried out over photocatalysts containing single (Pt or Cu) and bimetallic (Pt + Cu) co-catalyst loading onto TiO₂ with or without coating with ionic liquid after metal loading. Two tubular and one balloon photoreactor geometries were tested, and the balloon photoreactor geometry proved to be the most effective. Syngas was obtained as the main product using the single metal photocatalysts, while syngas and methane were obtained using the bimetallic photocatalyst. Using single metal loaded TiO₂, the maximum product yield obtained was 11.79 (with Pt) and 83.72 $\mu\text{mol}/(\text{h.gcat})$ (with Cu) for H₂ and CO, respectively. With the bimetallic photocatalyst, those values increased to 164.76, 1757.29, and 60.26 $\mu\text{mol}/(\text{h.gcat})$ for H₂, CO, and CH₄, respectively. Establishing better gas-photocatalyst contact in the photoreactor design and enhancing the properties of the photocatalyst by applying various modifications were proposed for future studies to further improve the system performance.

ÖZET

GAZ FAZDA FOTOKATALİTİK KARBON DİOKSİT İNDİRGEMESİ İÇİN ÇEŞİTLİ REAKTÖR GEOMETRİLERİNİN TASARIMI, YAPIMI VE TEST EDİLMESİ

Bu tez, karbondioksitin gaz fazında su ile fotokatalitik indirgenmesi için kapsamlı bir sisteminin tasarımına yönelik ön çalışmaları içermektedir. Çalışmada titanyum oksit bazlı fotokatalitik malzemelerin çeşitli ışık kaynakları kullanılacağı bir sistemin tasarlanması, yapımı ve çalıştırılması amaçlanmıştır. Bunu başarmak için, laboratuvar ölçekli sistem sıfırdan inşa edilmiş, cihazların kalibrasyonu yapılmış, fotokatalizörler sentezlenmiş ve sistemin bir bütün olarak çeşitli koşullarında ilk denemesi yapılmıştır, temel değişkenler olarak ışık kaynağının türü, katalizör miktarı, gaz akış hızları ve içinden CO₂ geçirilerek su buharı oluşturmak için kullanılan kabın sıcaklığı seçilmiştir. Reaksiyonlar, TiO₂'ye tek ve bimetalik eş katalizör yüklenmiş fotokatalizörler ve bunlara iyonik sıvı kaplanarak elde edilen malzemeler üzerinde gerçekleştirilmiştir. İki farklı tübüler ve bir balon olmak üzere üç farklı fotoreaktör geometrisi test edilmiş, balon fotoreaktör geometrisinin en etkili olduğu görülmüştür. Tek metal (Pt veya Cu) fotokatalizörleri kullanılarak ana ürün olarak sentez gazı elde edilirken, bimetalik (Pt + Cu) fotokatalizörler kullanıldığında sentez gazı yanında metan da elde edilmiştir. Tek metal yüklü TiO₂ kullanılarak elde edilen maksimum ürün verimi sırasıyla H₂ için 11.79 (Pt ile) $\mu\text{mol}/(\text{h.gcat})$, CO için ise 83.72 (Cu ile) $\mu\text{mol}/(\text{h.gcat})$ olmuştur. Bimetalik fotokatalizör ile bu değerler H₂, CO ve CH₄ için sırasıyla 164.76, 1757.29 ve 60.26 $\mu\text{mol}/(\text{h.gcat})$ olarak gerçekleşmiştir. Geliştirilmesi gereken alanları olarak, gaz-fotokatalizör temasını daha iyi sağlayacak reaktör tasarımı ve çeşitli modifikasyonlarla fotokatalizör özelliklerinin geliştirilmesi önerilmiştir.

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LIST OF SYMBOLS

E_g	Band gap energy
E_c	Conduction band energy
E_v	Valence band energy
E^0	Redox potential
e^-	Electron
ΔG	Gibbs free energy
H^+	Proton
h^+	Hole
k_B	Boltzmann constant

LIST OF ACRONYMS/ABBREVIATIONS

AQY	Apparent quantum yield
CB	Conduction band
DPU	Deposition precipitation with urea
GC	Gas chromatography
GHG	Greenhouse gas
IL	Ionic liquid
MFC	Mass flow controller
MMT	Montmorillonite
NBG	Narrow band gap
NOAA	National Oceanic and Atmospheric Administration
UV-Vis1	150 W solar simulator
UV-Vis2	300 W solar simulator
UV-Vis2 (F)	300 W solar simulator with focusing lens attachment
VB	Valence band
WB	Water bubbler
WBG	Wide band gap
WS	Water splitting

1. INTRODUCTION

Nowadays, a great deal of effort is being focused towards developing ways to ensure sustainable living conditions for upcoming generations. The term ‘environmental remediation’ refers to the process of mitigating or removing contaminants/pollutants from the air, soil, and water in the environment in order to protect ecosystems from further damages [1]. Environmental remediation is thus becoming one of the most significant notions that must be implemented for the realization of a sustainable future.

Carbon dioxide (CO_2) is the fourth most abundant component in dry air after oxygen, nitrogen, and argon [2]. According to the National Oceanic and Atmospheric Administration (NOAA) of USA, as of March 2023, the concentration of atmospheric CO_2 has risen to 419.55 ppm, corresponding to around an 8% increase in the last 10 years (Figure 1.1). This increase has been mainly attributed to human activities since the start of the industrial revolution in the 18th century [3].

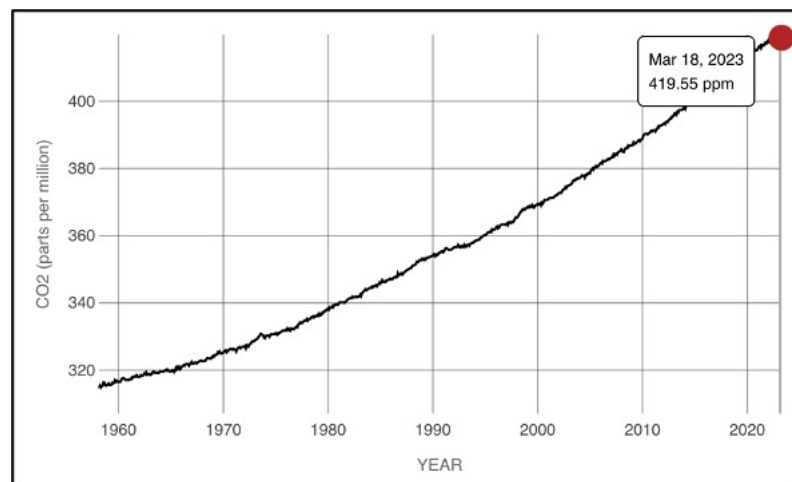


Figure 1.1. Atmospheric CO_2 levels. [3]

When in good balance, CO_2 plays a vital role in maintaining life on earth. It is also a key component in Earth’s carbon cycle, the process of reusing and recycling carbon throughout nature. As carbon represents the backbone of life on earth by regulating temperature, delivering food, and providing energy, CO_2 thus plays a big part in sustaining

life [4]. There are also many other advantageous uses for CO₂ like for freezing food, controlling chemical reactions, and dry cleaning [5]. However, as a main greenhouse gas (GHG), it traps heat in the atmosphere when it is discharged, especially through the burning of fossil fuels. The reckless and continuous release of GHGs leads to the excessive trapping of heat in the atmosphere, which in turn causes hazardous impacts on the climate and the survival of species worldwide [6]. As CO₂ makes up around two-thirds of overall GHG emissions, technologies for its capture, storage, and reutilization are becoming of utmost importance and are currently being widely studied and researched [7].

One of the ways in which CO₂ may be utilized for good is its use as an input for the production of other useful chemicals and products. This would decrease the harmful environmental impacts of the chemical industry by providing an alternative way of producing carbon-based fuels, reducing the dependency on fossil-fuel based sources, as well as producing other chemicals [9,10]. An interesting way of utilizing CO₂ is its photocatalytic reduction. This method, also known as artificial photosynthesis, transforms water (H₂O) and CO₂ into high-energy fuels upon light exposure [8]. In this thesis, the focus will be on a CO₂ reutilization process that photo-catalytically reduces CO₂ with H₂O vapor in a gas-phase system to mainly produce syngas and/or methane gas, which are valuable raw materials for energy production. Even though much research is being dedicated to this field, there are challenges that need to be overcome regarding photocatalyst selection, reaction mechanism, operating conditions, and reactor geometries. Main areas of research are now focused on the determination of new photocatalysts for CO₂ reduction, their characteristics, and their corresponding product yields [11].

The aim of this thesis therefore is to design, construct, and test a preliminary gas-phase system for the photocatalytic reduction of CO₂ with a focus on maximizing product gas yield using titania-based photocatalysts. A water bubbler was used to inject “moist” CO₂ (CO₂ + H₂O vapor) into the photoreactor, where the process of artificial photosynthesis took place upon irradiation by various sources of light. Titania (TiO₂), together with Pt and/or Cu cocatalysts were used as the semiconductor. The photocatalysts (semiconductor + cocatalyst) were also coated with ionic liquid to improve the charge transfer in some experiments. Two potential photoreactor geometries were constructed: a simple flow reactor and another balloon reactor, each operating under continuous flow. The simple flow reactor

(tubular) was investigated first using the various TiO_2 -based photocatalysts prepared. Then, the balloon reactor (round-shaped) was studied to compare the effect of the choice of reactor on the product yield; the effects of various operating conditions like amount of photocatalyst, flowrate, water vaporization temperature, and light source were also examined. Gases leaving the reactor passed through a Gas Chromatography (GC) unit, where they were identified and measured. Including this introductory chapter (Introduction), this thesis is comprised of five main chapters. Chapter 2 contains an extensive literature survey about the photocatalysis process and its application in CO_2 photoreduction. Chapter 3 presents the experimental details of the work, including photocatalyst synthesis and system process design. The obtained results are presented and discussed in Chapter 4, and then conclusions, challenges, and recommendations are summarized in Chapter 5.

2. LITERATURE REVIEW

2.1. Photocatalysis

From its name, photocatalysis is a process that uses photons (light) and a catalyst (semiconducting material) to initiate and accelerate a chemical reaction [1]. In general, the process involves the generation of an electron-hole pair in the semiconducting material when it is exposed to light. Semiconductors are usually defined based on their band gaps (E_g), which is the energy difference between the valence band (E_v) and the conduction band (E_c) of a material. Based on their ability to conduct electrons, each material has a unique band gap that characterizes its electron conducting performance [12], expressed as

$$E_g = E_c - E_v. \quad (2.1)$$

Based on the value of the band gap, E_g , a material is classified as either a conductor (metal), a semiconductor, or an insulator. Typically, a conductor has a band gap value of less than 1.0 eV, a semiconductor has a band gap value of less than 1.5-3.0 eV, and an insulator has a band gap value of more than 5 eV [12]. Figure 2.1 depicts these three types of materials.

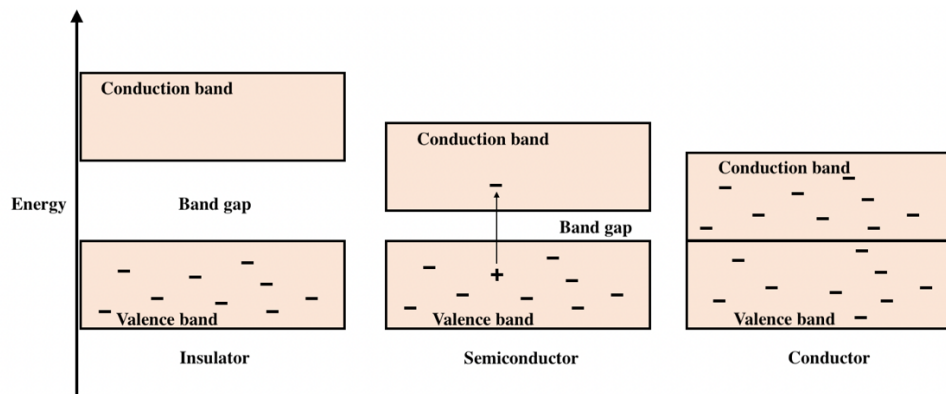


Figure 2.1. Band gaps of different types of materials. Adapted from ref. [12]

Figure 2.2 below shows a semiconductor where the band gap and the corresponding Gibbs free energy, G , is displayed.

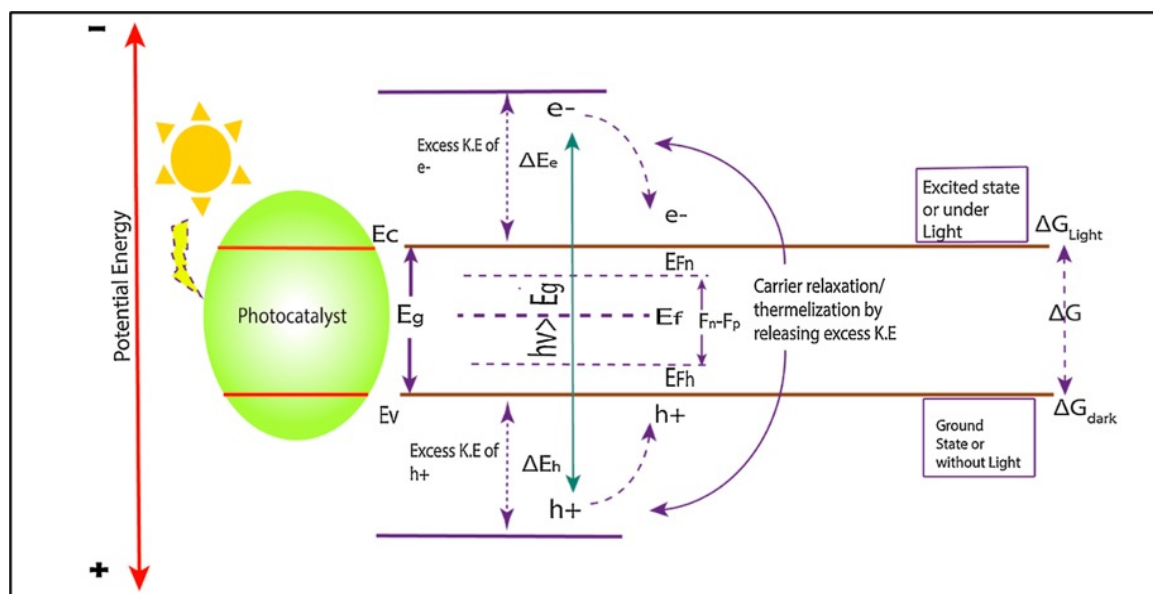


Figure 2.2. Semiconductor thermodynamics and Gibbs free energy with and without light.

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In photocatalysis, semiconductors work as photocatalysts because they can conduct electricity (electrons) at room temperature upon light irradiation. The process occurs when an electron (e^-) in the valence band absorbs the energy of the incoming photons from light and gets excited to the conduction band. A hole (h^+) is created in the valence band where the excited electron originally was, leading to the formation of a photo-excitation state with the generation of the e^- and h^+ pair [12]. This can only occur when the band gap of the photocatalyst is equal to or lower than the energy of the incident photon [15]. Photo-activation of the photocatalyst is said to have occurred when the e^- and h^+ pair is created [13, 14]. The e^- is used in the reduction of an acceptor while the h^+ is used in the oxidation of a donor. This is what makes photocatalysis important and advantageous, as the photocatalyst is able of providing a reduction and an oxidation environment at the same time [12]. Furthermore, there are other factors that make photocatalysis advantageous over other types of catalysis. Photocatalysis generally occurs at mild reaction conditions like sunlight irradiation, room temperature, and atmospheric pressure, making the conditions for the process readily available. Another advantage of photocatalysis is the presence of various

possibilities one can have as the photocatalyst. There are many different types of materials that have fitting band gaps and can act as a photocatalyst, which makes the process flexible and cost-friendly [1].

At the same time, there are potential problems regarding charge separation and transfer that may occur and lead to energy loss rather than initiation of a surface reaction. These problems involve the occurrence of volume and surface recombination. Volume recombination occurs when the generated electron-hole pair recombines in the bulk of the semiconductor instead of being transferred to the adsorbed species, while surface recombination takes place when the pair recombines on the semiconductor surface [13]. Figure 2.3 presents a schematic of the photocatalysis process with the possible cases mentioned just above.

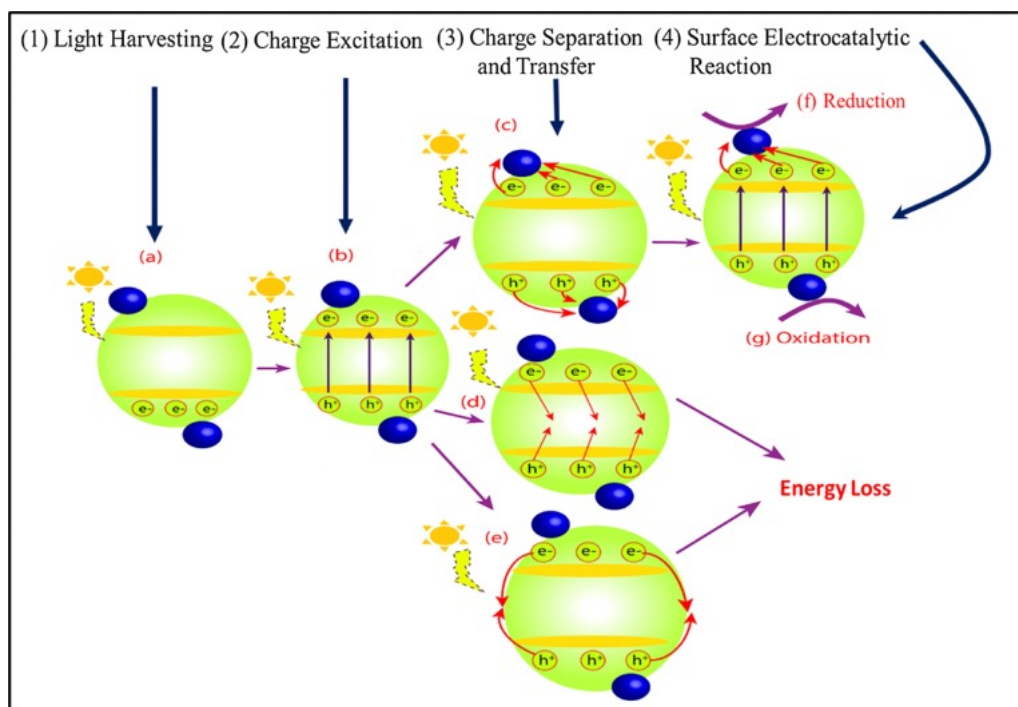


Figure 2.3. Photocatalysis process and possible outcomes. Reproduced from ref. [13] with permission from Elsevier copyright, 2019.

The recombination cases shown in (d) and (e) in Figure 2.3 generally occur when electrons cannot find trapped sites or if the band gap of the semiconductor is too small. This causes the electron-hole pairs to recombine and generate thermal energy. To avoid this and

increase photoactivity, charge trapping is required [16]. Shortening the diffusion length of the charge carriers or constructing interfacial electric fields can also help in avoiding the recombination [13]. Also, adjusting the photocatalyst itself by means of various modification methods helps in generating more efficient photoactivity and reducing such unwanted effects. For example, modifications like doping/loading with metals or other compounds adjusts the band gap range of the photocatalyst and gives it a higher conductive advantage (see section 2.3 about properties of photocatalysts).

As depicted in Figure 2.2, photo-activated e^- and h^+ created in the photocatalyst can “relax” through thermal generation by releasing excess kinetic energy to arrive at a quasi-equilibrium state. The quasi-fermi levels of the e^- ’s and h^+ ’s, which are the states of e^- and h^+ that have the potential to become involved in chemical reactions [13, 14], are expressed as

$$F_n = E_c + k_B T \ln \frac{n}{N_c}, \quad (2.2)$$

$$F_p = E_v + k_B T \ln \frac{p}{N_v}, \quad (2.3)$$

where E_c and E_v are the conduction and valence energy band positions, k_B is the Boltzmann constant, T is the thermal absolute temperature, n and p are electron and hole concentrations, and N_c and N_v are the effective densities of states at the conduction and valence energy band levels. The band gap energy of thermally induced e^- ’s and h^+ ’s is measured using

$$\frac{E_g}{k_B T} = - \ln \frac{n_0 p_0}{N_c N_v}, \quad (2.4)$$

where n_0 and p_0 are concentrations of the thermally induced e^- ’s and h^+ ’s, respectively [13]. Equation (2.4) comes from the fact that thermally induced e^- ’s and h^+ ’s follow the Boltzmann distribution, making their product a constant [14].

The maximum thermodynamic force needed for the e^- 's and h^+ 's to induce photocatalytic reactions in the presence of light having energy greater than E_g [13,14] is measured using

$$\Delta G = G_{\text{dark}} - G_{\text{light}} = -|F_n - F_p| = -E_g - k_B T \ln \frac{n_p}{N_c N_v}. \quad (2.5)$$

If Equation (2.4) is substituted into Equation (2.5) under thermal equilibrium conditions, ΔG becomes zero, which indicates that heat cannot induce photocatalytic reactions. However, with light excitation, a difference between G_{light} and G_{dark} gibbs free energies results, which causes electrons to transfer from the valence band to the conduction band to start photocatalysis [13]. Heterogeneous photocatalysis, where the photon-initiated reactions occur at the interface between a solid photocatalyst and a liquid or gas reacting medium, is an ideal method of getting rid of contaminants in air and water [1], and thus is readily used for processes like CO_2 photoreduction.

2.2. Photocatalytic CO_2 Reduction

The surface reactions shown in the fourth step in Figure 2.3 from the previous section are the ones directly responsible for CO_2 conversion into products. With the help of a reducing agent that enters the system alongside CO_2 as the second reactant, CO_2 can be reduced to give a variety of products, as there are many different possible reactions that can take place. These generally depend on the operating conditions, whether the system is being operated in the gas or liquid phase, and the choice of reductant used. This is because the oxidation of the reductant also provides intermediates that take part in the reactions occurring in the system. Water, H_2O , or pure hydrogen, H_2 , are the two reductants mainly used for CO_2 photocatalytic reduction. However, sometimes methane, CH_4 , and methanol, CH_3OH , are used when producing hydrocarbons is the main goal. In general, H_2 and H_2O lead to the formation of C_1 products, while CH_4 and CH_3OH are said to lead to the formation of C_2 and C_3 products. In all cases, the formation of the $\text{CO}_2^{\cdot-}$ anionic radical is the first step. If an acidic metal oxide like TiO_2 is used (see subsection 2.3.1 about TiO_2 photocatalyst), the anion radical forms as a result of the physisorbed interaction between CO_2 and the surface of the photocatalyst. Experimental reports also show that basic metal oxide photocatalysts like ZrO_2 , MgO , and Ga_2O_3 can be used and have shown chemisorbed interactions with CO_2

[13, 16]. Table 2.1 shows the first step of the formation of the anionic radical, as well as some other possible products that may be produced with the reaction of the e^- and the h^+ with CO_2 .

Table 2.1. Possible reactions and their redox potentials at 25 °C. Reproduced from ref. [13] with permission from Elsevier copyright, 2019.

Reaction Type	Redox Potential $E^0(V)$ vs NHE at pH=7
$CO_2 + e^- \rightarrow CO_2^-$	-1.90
$2CO_2(g) + 2H^+ + 2e^- \rightarrow HCO_2H(aq)$	-0.61
$CO_2(g) + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
$CO_2(g) + 4H^+ + 4e^- \rightarrow C(s) + 2H_2O$	-0.2
$CO_2(g) + 4H^+ + 4e^- \rightarrow HCHO(aq) + H_2O$	-0.48
$CO_2(g) + 6H^+ + 6e^- \rightarrow CH_3OH(aq) + H_2O$	-0.38
$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O$	-0.24
$2CO_2(g) + 8H_2O + 12e^- \rightarrow C_2H_4(g) + 12OH^-$	-0.34
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	-0.27
$2CO_2(g) + 9H_2O + 12e^- \rightarrow C_2H_5OH(aq) + 12OH^-$	-0.33
$3CO_2(g) + 13H_2O + 18e^- \rightarrow C_3H_7OH(aq) + 12OH^-$	-0.32

Figure 2.4 shows the number of electrons (e^-) for reduction, holes (h^+) for oxidation, and protons (H^+) needed to form possible products in CO_2 photocatalysis from CO_2^- [16].

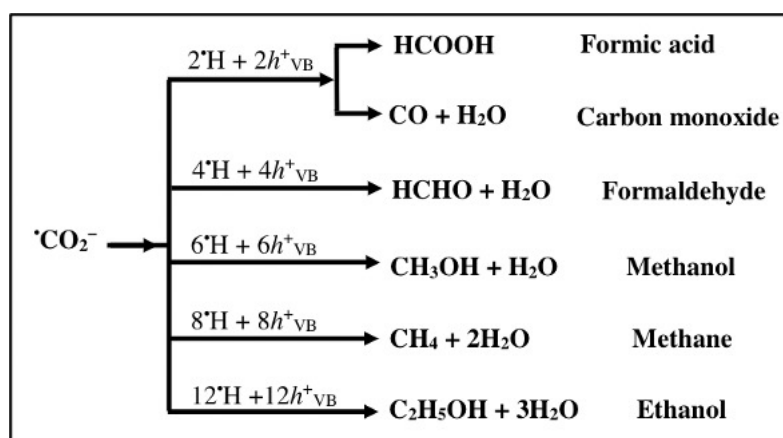
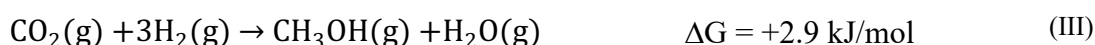
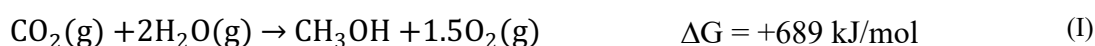


Figure 2.4. Possible product forming pathways. Reproduced from ref. [16] with permission from Elsevier copyright, 2016.

Besides the tendency towards forming different products, there are certain benefits and limitations that come with each choice of reductant. When H_2 is used, the process is usually referred to as CO_2 methanation. Higher yield rates are expected through photoreduction with H_2 directly. Additionally, reactions with CO_2 and H_2 are more thermodynamically feasible than those of CO_2 and H_2O , which can be seen by comparing the Gibbs free energy change of the reactions [16].



The reaction shown in (IV) involving the production of methane is the most thermodynamically feasible, as is seen by its large negative Gibbs free energy change value. This reaction is also called the Sabatier reaction. It is exothermic and can be catalyzed by nickel in the dark at moderate temperatures. It can also be initiated through photocatalysis at room temperature. However, as the temperature increases with reaction progression, a combination of catalytic and photocatalytic processes may occur. Therefore, temperature is an important parameter that must be recognized in $CO_2 + H_2$ photocatalysis [16].

For H_2O , advantages include being naturally available and abundant, and being an inexpensive source of hydrogen. As a product, hydrogen is valuable in syngas and as a precursor for useful chemical products, including those that are carbon-based. However, there are some limitations to using H_2O as the reductant in the reduction of CO_2 . When H_2O is used, photocatalytic water splitting occurs when H_2O adsorbs on the surface of the photocatalyst. The formation of H_2 from water splitting becomes more favorable from a kinetics point of view than the formation of CO_2 reduction products, causing competitive reactions [11]. Although hydrogen can also be formed as a product of CO_2 reduction, it is usually then readily consumed again to form CH_4 . Thus, when H_2O is used as the reductant, the process usually takes place in two steps: 1) water splitting to produce hydrogen and then 2) CO_2 methanation to produce methane. Different operating conditions and types of photocatalysts can be used to adjust the reaction mechanism towards the formation of specific products. Furthermore, due to the high polarity of H_2O , it is more likely to be

adsorbed on the photocatalyst surface instead of CO₂, which has a lower dipole moment, and take up more space on the surface. However, this may be fixed by creation of photocatalysts with oxygen vacancy sites to enhance CO₂ adsorption or by adjusting the amount of H₂O flowing in the system [16]. Even so, another limitation of using H₂O is the oxygen released from its oxidation, which may slow down the photocatalytic activity and even lead to the reverse formation of CO₂. Using H₂ directly is more advantageous in this respect due to the lack of oxygen [11].

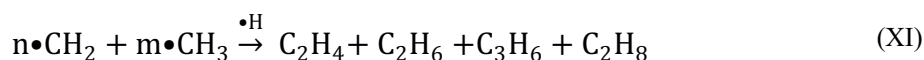
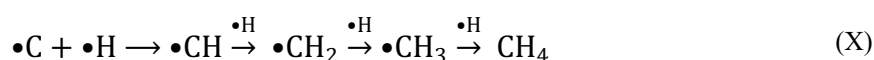
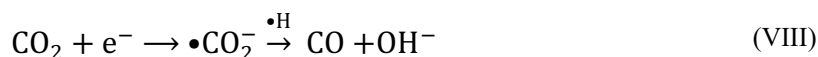
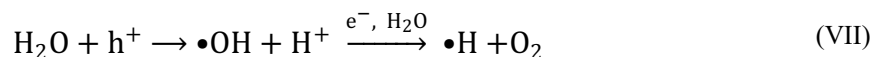
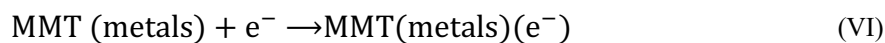
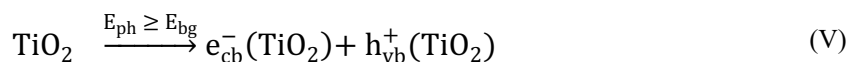
It is worth noting that when H₂O is used, the reduction of CO₂ does not follow the same pathway in both liquid and vapor water systems. Table 2.2 constructed by Karamian & Sharifnia provides a summary of the main products in each system [16]. In general, many references indicate that carbon monoxide, CO, and CH₄ are the main products in gas-phase systems, while CH₃OH, CH₃COOH, and HCOOH are the main products in liquid phase systems [17]. Table 2.2 summarizes some products under either liquid or gas phase systems using different photocatalysts.

Table 2.2. Summary of CO₂ photocatalysis with H₂O using different photocatalysts.

Reproduced from ref. [16] with permission from Elsevier copyright, 2016.

Photocatalyst	Reactants		Light source	Major Product
	CO ₂	H ₂ O		
ZnO	Saturated	Liquid (100 mL)	500 W Xe/HP Hg	HCHO, CH ₃ OH
GaP	Saturated	Liquid (100 mL)	500 W Xe/HP Hg	HCHO, CH ₃ OH
CdS	Saturated	Liquid (100 mL)	500 W Xe/HP Hg	HCHO, CH ₃ OH
TiO ₂	Saturated	100 mL, 0.1 N NaOH	500 W W-halogen	HCOOH
TiO ₂ (P25)	Gas	Gas	UV (365 nm)	CH ₄
N ₃ dye-0.5 wt% Cu- 0.5 wt% Fe-TiO ₂	Saturated	Water vapor	Concentrated natural sunlight (20 mWcm ⁻²)	CH ₄
ZnS/MMT	Saturated	0.2 M NaOH solution	8 W Hg lamp (254 nm)	CH ₃ OH, CH ₄
CdSe-Pt/TiO ₂	Gas	Gas	300 W Xe (> 420 nm)	CH ₄ , CH ₃ OH
PbS-Cu/TiO ₂	Gas	Saturated vapor	300 W Xe (UV cut)	CO, CH ₄
Cu-TiO ₂	Saturated	300 mL, 0.2 N NaOH	Hg (254 nm)	CH ₃ OH
HNb ₃ O ₈	Saturated	Water vapor (7 kpa)	350 W Xe lamp	CH ₄
TiO ₂	Saturated	Saturated vapor	UV light (253.7 nm)	CH ₄
TiO ₂ (Anat.)	Saturated	Liquid (57.5 mL)	990 W Xe lamp (340 nm)	HCOOH
Cu-Fe/TiO ₂ -SiO ₂	Gas (0.72 bar)	Vapor (0.72 bar)	150 W Hg and solar light	CH ₄ , C ₂ H ₄

There are several studies in the literature that explain the reaction mechanism of the process with H₂O using TiO₂ as a photocatalyst. In one of the many works done by Tahir et al., the following chemical equations representing all the possible reaction steps occurring in photocatalytic CO₂ reduction with H₂O using TiO₂ modified with a montmorillonite (MMT) support are given [18].



The reactions display the steps in which CO_2 is reduced and H_2O is oxidized. First, light irradiating on the catalyst surface produces the electron hole pairs in the conduction and valence bands respectively, as discussed in the previous subsection. The MMT support used in this mentioned work acted as a medium for trapping electrons to further promote the photocatalysis. Doping TiO_2 with other metals like Pt, Cu, Au, etc. also accomplishes this goal. The electrons generated are responsible for the photoreduction of CO_2 into $\bullet\text{CO}_2^-$ radicals while the holes are responsible for the photooxidation of H_2O into the hydroxyl radical, $\bullet\text{OH}^-$, and hydrogen ions, H^+ . Oxidizing H_2O further with $\bullet\text{OH}^-$ generates O_2 and H^+ once more. The reduction of the H^+ ion with an e^- gives the hydrogen radical, which reacts with the carbon dioxide on the catalyst surface to form CO and with the subsequently produced carbon radicals to generate hydrocarbon intermediates until CH_4 is created [18].

The generation of products from photocatalytic CO_2 reduction can also be clarified using the energy band theory. Table 2.1 on page 9 showed the redox potentials for the chemical reactions involved in the process with reference to NHE at a pH of 7. The energy band theory is based on the relative positions of the conduction and valence bands and the redox potentials. Generally, if the redox potential, E^0 , of a certain reaction is below the conduction band potential of the semiconductor (i.e., photocatalyst), the excited electrons can be efficiently consumed in the reaction [18]. Figure 2.5 on the next page displays the redox potentials and band gap energies of some photocatalysts for reference.

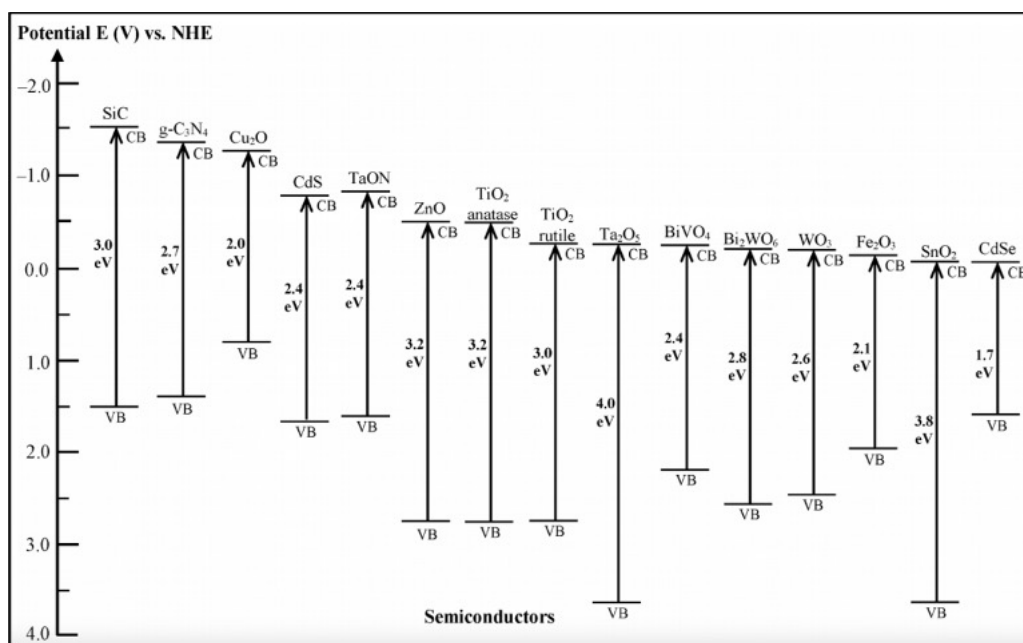


Figure 2.5. Selected semiconductor band gaps and redox potentials. Reproduced from ref. [19] with permission from MDPI copyright, 2021.

As can be seen from Figure 2.5, the conduction band potential of TiO_2 , E_{CB} , is around -0.5 V , allowing the electrons in the conduction band to have enough energy for the reactions generating the main gas products: H_2 , CO , and CH_4 [20].



From the reactions shown above, it is clear that the reaction involving the production of methane is well within the energy range and can be actualized. Furthermore, the redox potentials show that the production of methane is thermodynamically more feasible than the production of H_2 or CO . However, it is also important to note that hydrogen evolution is kinetically more feasible, as the production of CH_4 requires 8 electrons instead of 2 [20].

The basic process is summarized in Figure 2.6.

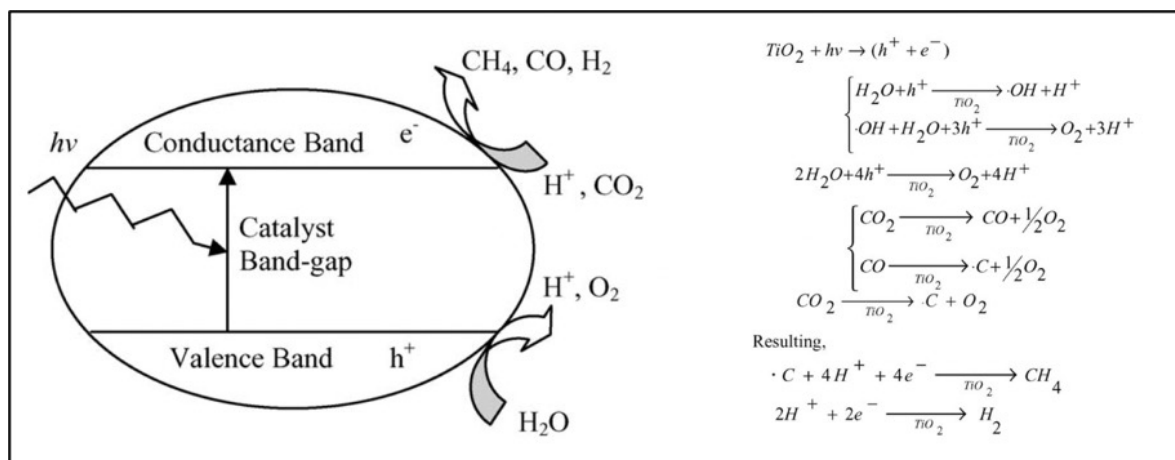


Figure 2.6. Schematic and reaction scheme of CO₂ photocatalytic reduction on TiO₂ pellets. Reproduced from ref. [20] with permission from Elsevier copyright, 2012.

Therefore, since the energy band gap of the photocatalyst plays an important role in its photocatalytic activity, the selection and enhancement of the photocatalyst in terms of modifications is very important in this field of research. This is further discussed in the next section.

2.3. Properties and Modifications of Photocatalysts

In nature, CO₂ is a very stable chemical compound with strong C=O double bonds (high bond enthalpy of +750 kJ/mol). Hence, the breaking down of CO₂ is a process that requires inputting high amounts of energy. Moreover, since CO₂ is optically inert under UV and visible light, adjusting the photocatalyst to fit the desirable band gap for CO₂ to undergo the photocatalytic reactions is very important [13]. Thus, the choice of photocatalyst is significant to the overall effectiveness of the process, as it also affects factors like the undertaken reaction pathway, the type of light absorbed, and the possible products to be formed. Metal oxide semiconductors, nitrides, sulfides, carbides, carbonaceous materials, dyes, quantum dots, and enzymes are types of materials that have been researched as photocatalysts. Metal oxides, specifically, have been extensively reported on throughout the literature for having promising photocatalytic properties [21]. Those include titanium

dioxide (TiO_2), tungsten trioxide (WO_3), zinc oxide (ZnO), zirconium oxide (ZrO_2), cerium (IV) oxide (CeO_2), iron (III) oxide (Fe_2O_3), tin (IV) oxide (SnO_2) and others [19, 21]. Figure 2.7 shows the band energy of some selected photocatalyst in terms of being favorable or unfavorable with respect to the water splitting and CO_2 reduction processes. As highlighted in the previous section, if the CB energy level is more negative than the reduction reactions' energy and the VB energy level is more positive than the oxidation reactions' energy, then the photocatalyst has a favorable band alignment [22].

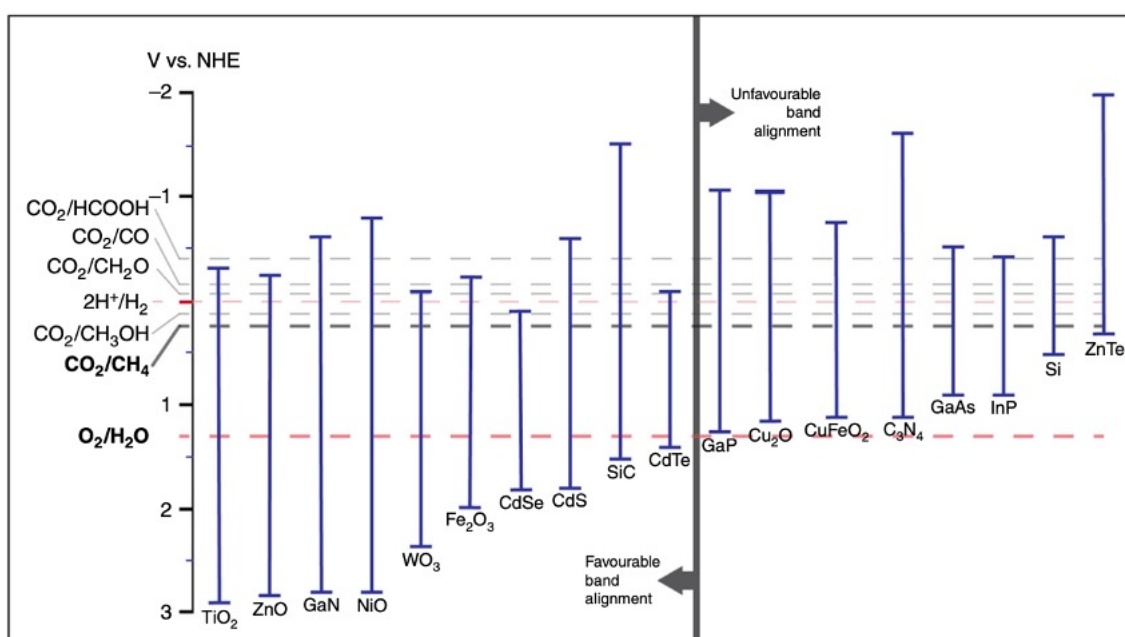


Figure 2.7. Band alignments of selected semiconductors. Reproduced from ref. [22] with permission from Springer Nature copyright, 2019.

As Figure 2.7 also indicates, the photocatalysts like TiO_2 and ZnO are wide band gap (WBG) semiconductors, as opposed to narrow band gap (NBG) semiconductors like CdSe and CdTe . WBG and NBG semiconductors differ in the type of light they need to absorb for photoexcitation to take place. The most commonly used photocatalysts are generally WBG semiconductors, and they require irradiation by UV light of short wavelength. As visible light radiation makes up a large amount of the solar spectrum, WBG semiconductors thus do not efficiently make use of solar energy. Also, although WBG semiconductors provide the required amount of energy for redox reactions, they are more susceptible to undergo recombination due to the larger gap. Hence, the chosen photocatalyst must be a WBG

semiconductor to ensure redox reactions, but it must also be modified in such a way so that the solar spectrum could be used more effectively, and recombination could be prevented [23]. Overall, two main requirements of a good photocatalyst are: 1) being able to transfer multiple electrons from the photocatalyst to CO_2 , and 2) the consumption of the generated holes by the oxidation reactions as to avoid accumulation of holes that could lead to recombination [13]. In the subsections to come, some modifications that may be applied to achieve the required criteria mentioned are presented. As depicted in Figure 2.8, TiO_2 , alongside ZnO , is one of the most researched and used semiconductors in photocatalysis [24]. Therefore, in this thesis, the main focus is on TiO_2 based photocatalysts and its modifications.

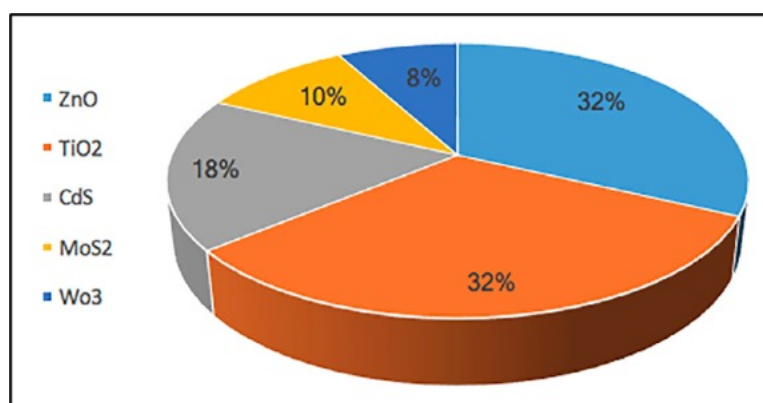


Figure 2.8. Publications using different semiconductors for photocatalysis. Reproduced from ref. [24] with permission from Hindawi copyright, 2020.

The next subsection focuses on TiO_2 as a photocatalyst by presenting its structure, characteristics, as well as the main advantages and disadvantages of its photocatalytic properties.

2.3.1. TiO_2 as a Photocatalyst

Titania, or titanium dioxide, TiO_2 , is an intrinsically n-type semiconductor that has three crystal forms in nature: brookite, anatase, and rutile. It is an n-type semiconductor by nature because of the oxygen vacancies that could be created to provide electrons. However, it is good to note that it could also have p-type semiconductivity upon doping with specific

elements (see subsection 2.3.2). Table 2.3 displays the phase transformation temperatures of TiO_2 [25], while Figure 2.9 displays the crystal structures of the three main TiO_2 polymorphs [26].

Table 2.3. TiO_2 phase transformation temperatures. Reproduced from ref. [25] with permission from Springer copyright, 2020.

Phase transformation	Phase transformation temperature	Reference
Brookite-rutile	500–600°C	[1]
	800°C	[2]
Anatase-rutile	850°C	[3–5]
	250°C (4000 kPa)	[6]
	680°C	[7]
	620°C (dry environments)	[8]
	570°C (humid argon)	[8]

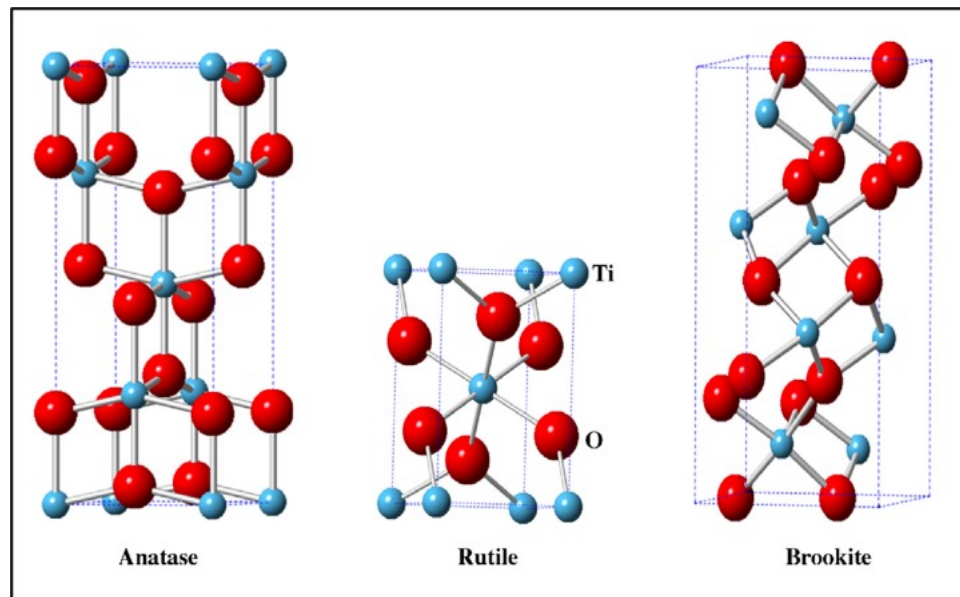


Figure 2.9. Anatase, rutile, and brookite TiO_2 crystal structures. Reproduced from ref. [26] with permission from Elsevier copyright, 2015.

The crystal structures shown in Figure 2.9 indicate that the basic unit composing TiO_2 is a TiO_6 octahedron, as each Ti atom is attached to 6 oxygen atoms, forming an octahedron-shaped unit geometry. For each crystal structure, the TiO_6 octahedrons are connected differently and have different shape distortions. For anatase, an edge is shared by adjacent octahedrons. For rutile, one corner is shared by adjacent octahedrons, which are arranged

with the long axis alternating by 90° . In the case of brookite, it is composed of octahedrons sharing a corner and an edge [25]. However, brookite is not widely used, as it is quite unstable at room temperatures [27]. Anatase and rutile are the crystal forms that were used more commonly; the main difference between them is how their octahedrons are distorted and connected. Anatase has a tetragonal structure with dipyramidal distortion, and each octahedron is connected to another 8 adjacent octahedrons. Rutile also has a tetragonal crystalline structure but with prismatic distortions. The octahedrons in rutile are assembled in parallel chains and they are somewhat distorted, and each octahedron is connected to another 10 adjacent octahedrons. Rutile has shorter Ti-Ti and longer Ti-O distances than anatase [25, 27]. The different crystal structures provide TiO_2 with different and distinct chemical and physical properties, which are summarized in Tables 2.4 and 2.5.

Table 2.4. X-ray data for TiO_2 structure. Reproduced from ref. [25] with permission from Springer copyright, 2020.

Crystal structure	System	Space group	Lattice constants/nm			
			<i>a</i>	<i>b</i>	<i>c</i>	<i>c/a</i>
Rutile	Tetragonal	$D_{4h}^{14} - P4_2/mnm$	0.4584	–	0.2953	0.644
Anatase	Tetragonal	$D_{4h}^{19} - I4_1/amd$	0.3733	–	0.937	2.51
Brookite	Rhombohedral	$D_{2h}^{15} - Pbca$	0.5436	0.9166	0.5135	0.944

Table 2.5. Chemical and physical properties of TiO_2 . Reproduced from ref. [25] with permission from Springer copyright, 2020.

	Anatase	Brookite	Rutile
Density/(g/cm ⁻³)	3.83	4.17	4.24
Melting point/°C	Turning into rutile		1870
Boiling point/°C	2927 (at pressure pO ₂ 101.325 kPa)		
Band gap/eV	3.2	–	3
Refractive index			
<i>n_g</i>	2.5688	2.809	2.9476
<i>n_p</i>	2.6584	2.677	2.6506
Dielectric properties	55	78	110–117
Hardness on mineralogical scale (Mohs scale)	5–6.5		

Due to the suitability of its properties, TiO_2 can be used in a variety of applications like solar cells, capacitors, paint pigments, as well as food coloring agents. As the anatase form has the highest band gap, it has the highest oxidative potential and photocatalytic activity. Also, it has high surface area, it is non-toxic, and it is more photochemically stable. Thus, the anatase form of TiO_2 is mainly used, and combinations of the anatase and rutile forms are also popular. As a photocatalyst, the listed properties have made TiO_2 one of the

most extensively used materials in photocatalysis. Not only because of its high oxidative efficiency and low toxicity, but also due to its availability at low cost and its capacity to resist photo-corrosion [20]. However, along with its advantages, there are also disadvantages and problems regarding TiO_2 as a photocatalyst. Like previously stated, TiO_2 is a WBG semiconductor, which means that it can only make use of the 5% accounting for UV radiation in the solar spectrum. This is poor utilization of solar energy. Also due to its large band gap, TiO_2 can experience very rapid e^-/h^+ recombination, slowing its reaction rate. Thus, significant amount of research has been going towards enhancing TiO_2 with different modifications, such as metal/non-metal doping, dye sensitization, creating composites with other materials, and more [25].

2.3.2. TiO_2 Photocatalyst Modifications

The most commonly used modification methods to enhance the photocatalytic performance of TiO_2 are briefly described in this subsection.

2.3.2.1. Doping. Doping is the process of adding foreign metal or non-metal ions (dopant) to the crystal lattice of a semiconductor. Doping generates either a p-type (more positive) or n-type (more negative) semiconductor depending on the type of dopant used. If the dopant has a higher valency than the semiconductor n-type doping occurs. Likewise, p-type doping occurs when the dopant element has a lower valency. It is important to note that dopant ions must have an atomic size very similar to the size of the ones being substituted for efficient doping without distortions [23]. Doping enhances the photocatalyst optically to include more of the solar spectrum and it also helps in repressing charge carriers so that rapid recombination does not occur [24]. Thus, doping introduces defects to the crystal lattice of the semiconductor that modify its electronic structure. These defects create trap sites to catch the electrons and holes generated after photoactivation. Additionally, the defect sites and the oxygen vacancies created increase the catalytic activation of strong bonds, which kinetically improves the reactions. Overall, doping affects light absorption wavelengths, reduces recombination using trap sites, and changes the conduction and valence energy band positions to either widen or narrow the band gap of the chosen photocatalyst [23]. In the case of TiO_2 , being a WBG semiconductor, doping would narrow its bandgap so that more of the visible light in the solar spectrum could be absorbed. For example, it is reported that doping

TiO₂ with Ag metal species allows the photocatalyst to have better solar utilization due to the surface plasmon resonance effect present in the visible light spectrum [25]. Co-doping is also possible, where pairs of either metal-metal, metal-nonmetal, or nonmetal-nonmetal are established. For metal-nonmetal co-doping, the metal induces the transfer of charge carriers while the nonmetal increases visible light absorption. This type of co-doping narrows the overall bandgap results in two different heterostructures with respect to TiO₂. In co-doping, it is important to choose an effective pair and to keep in mind the weight of dopants and by which method they are introduced. The co-doping process is also reported to be effective due to the related synergistic effects that come along with it [20].

2.3.2.2. Surface Sensitization. Surface sensitization is another modification used to enhance the photocatalytic activity of TiO₂. Since the chemisorbed or physisorbed sensitizers on TiO₂ are much more easily excited than TiO₂ itself, the photoexcitation process could be significantly improved and more efficient. The sensitizers also help in extending the excitation energies so that the visible region of the solar spectrum is included [25], as they can harvest visible light and introduce the photoexcited electrons into the conduction band of TiO₂. Sensitizers are usually organic dyes, and many have been reported to be used to modify TiO₂ in the literature. These dyes include rhodamine B, thionine, porphyrins, eosin, and carbocyanines [20].

2.3.2.3. Creating Composites. The coupling of different kinds of semiconducting materials having distinct energy band gaps is another modification technique. Again, this expands the absorption spectrum and provides effective carrier separation. A WBG semiconductor like TiO₂ could be coupled with NBG semiconductors to induce its photoactivation. Also, due to the addition of charge from the conduction band of the NBG semiconductor to the conduction band of TiO₂, much more efficient charge separation can be achieved, reducing e^-/h^+ recombination. For example, creating a composite photocatalyst composed of anatase and rutile forms of TiO₂ has been reported to show better photocatalytic activity than pure anatase. This is due to the lower recombination rate achieved from the transfer of electrons from anatase to rutile [25]. Another example of coupled semiconductors is the heterostructured Cu₂O-TiO₂ photocatalyst. Cu₂O is a typical NBG semiconductor with a band gap of 2.0 eV. Both its CB and VB are above those of TiO₂, making the transfer of photoexcited electrons and holes between the two Materials thermodynamically favorable. It has been

reported that composites with 30% and 70% Cu₂O give 6 and 27 times higher photoactivity under both UV and visible light radiations compared to TiO₂ alone. Other NBG semiconductors have also been reported to form advantageous heterostructures with TiO₂ like PbS, CdS, and CdSe [20].

2.3.2.4. Modifications in Physical Properties. Modifications in the physical properties of TiO₂ like control of particle size, as well as adjusting morphology, pore structure, and spatial structure can additionally lead to improvements in its photoactivity. In terms of morphology, TiO₂ can be formed in different shapes like nanosheets, nanobelts or foams, while for pore structure it is effective to have an ordered mesoporous structure. Likewise, in terms of spatial structure, having TiO₂ nanotubes proved to be very advantages. These physical properties help improve photoactivity by providing high surface area and efficient charge separation. Several studies reported on the effectiveness of the encapsulation of nanoscale TiO₂ clusters into nano-sized cavities of other materials, such as zeolites. Moreover, both ordered mesoporous TiO₂ (having high surface area and pore volume) and nanosized TiO₂ dispersed on mesoporous silica matrix have been researched for their high photoactivity in the reduction of CO₂ [20].

2.3.3. TiO₂-Based Photocatalysts in CO₂ Reduction

This subsection presents a review of some of the various modified TiO₂ photocatalysts available in the literature used in the photocatalytic reduction of CO₂.

Table 2.6. Summary of some modified TiO₂-based photocatalysts in CO₂ photoreduction.

Modified Photocatalyst	Remarks	Ref
Pt ²⁺ – Pt ⁰ /TiO ₂ nanoparticles	- Improved yield of H₂ and CH₄ - Low recombination rate caused by Pt nanoparticles - Strong visible light absorption and high surface area due to Pt²⁺ ions	[28]

Table 2.6. Summary of some modified TiO₂-based photocatalysts in CO₂ photoreduction (cont.).

Hybrid Cu _x O–TiO ₂ Heterostructured Composites	- Intrinsic p-n heterojunction material gave greater light absorption and rapid charge separation. - Heterostructured photocatalyst showed improvements in photocatalytic activity. - Methane yield of 221.63 ppm·g⁻¹·h⁻¹ is achieved without employing any metals.	[29]
CdS/TiO ₂ nanocomposite	- The optimal weight ratio and average crystal size of CdS is 45% and 13 nm.	[30]
Pd–TiO ₂	- Experimental data showcased that CO₂ and CO₃²⁻ are the main carbon sources of the CH₄ formation, which takes place on the Pd site of Pd–TiO₂.	[31]
Blue colored Pt-sensitized reduced TiO ₂	- Actively promotes CO₂ photoreduction under solar spectrum light. - Optimized samples gave a maximum CH₄ yield of 80.35 μmol g⁻¹ h⁻¹ and a 12.40% apparent quantum yield (AQY).	[32]
Blue colored reduced TiO ₂ sensitized with bimetallic Cu–Pt nanoparticles	- Generated both methane and ethane under artificial sunlight (AM1.5). - Photoconversion efficiency of 1%, with an AQY of 86%. - Copper adsorbs CO₂, while Pt nanoparticles act as electron scavengers that prevent e⁻/h⁺ recombination. - The synergistic effects of the bimetallic nanoparticles on the reduced TiO₂ significantly increase photoconversion efficiencies. - The results show the importance of oxygen vacancies and the positioning of the bimetallic nanoparticles.	[33]
Black TiO ₂ nanotubes	- The formation of black NTs was realized with a stainless-steel reactor at high temperatures and under flow of H₂. - The choice of reaction conditions plays a major role in the characteristics of the resulting material.	[34]
Pt-TiO ₂ nanostructured films (1D structure of TiO ₂ crystals coated with ultrafine Pt NPs (0.5-2 nm))	- Selective generation of methane (max. CH₄ yield of 1361 μmol/g-cat/h) - Rapid e⁻ transfer rate in TiO₂ crystals and effective e⁻/h⁺ separation by Pt nanoparticles. - Importance of size of nanoparticles and the structure of 1D film of TiO₂ single crystals.	[35]
Pt on hierarchically ordered TiO ₂ – SiO ₂ (HTSO) porous materials	- Decreasing the size of Pt NPs helps improve the charge transfer efficiency but causes selectivity towards hydrogen instead of methane. - Unsensitized TiO₂-SiO₂ had a CH₄ production rate of 45 nmol/gh.	[36]

Table 2.6. Summary of some modified TiO₂-based photocatalysts in CO₂ photoreduction (cont.).

Pt-TiO₂ nanostructured films (1D structure of TiO₂ crystals coated with ultrafine Pt NPs (0.5-2 nm))	- Selective generation of methane (max. CH₄ yield of 1361 μmol/g-cat/h) - Rapid e⁻ transfer rate in TiO₂ crystals and effective e⁻/h⁺ separation by Pt nanoparticles. - Importance of size of nanoparticles and the structure of 1D film of TiO₂ single crystals.	[35]
Pt on hierarchically ordered TiO₂-SiO₂ (HTSO) porous materials	- Decreasing the size of Pt NPs helps improve the charge transfer efficiency but causes selectivity towards hydrogen instead of methane. - Unsensitized TiO₂-SiO₂ had a CH₄ production rate of 45 nmol/gh.	[36]
TiO₂-graphene hybrid nanosheets	- Abundant Ti³⁺ is found on the surface of TiO₂ of the hybrid, which serve as sites for trapping e⁻/h⁺ pairs. - The generation of C₂H₆ is favored based on the synergistic effect of the surface-Ti³⁺ sites and graphene. - Yield of C₂H₆ increases with the amount of incorporated graphene.	[37]
TiO₂-CIS	- Demonstrates the highest selectivity for ethane (>70%) and a higher efficiency of converting UV radiation into fuels (4.3%) using concentrated sunlight compared with platinum doped TiO₂ nanoparticles (2.1%). - Utilize hot electrons to tune the solar fuel from alkanes to aldehydes.	[38]
Mesoporous TiO₂ modified with bimetallic Au/Cu nanostructures	- The bimetallic TiO₂/Au/Cu display higher photoreduction activity of CO₂ than the monometallic TiO₂/Au and TiO₂/Cu. - Greatest methane formation at an optimal 1:3 gold-copper mole ratio. - The activity depends on the method of metal deposition on the semiconductor surface. The greatest rate for methane formation is found for initial gold deposition followed by deposition of copper.	[39]
Montmorillonite (MMT) dispersed Fe/TiO₂ nanocatalyst (MMT-clay supported Fe/TiO₂ dip-coated over monolith microchannels)	- Cordierite monolithic support improves photo-activity and reusability of Fe-MMT/TiO₂ nanocomposite. - Obtained much higher CO amount due to larger surface area. - A maximum CO yield of 166 mmole g-cat⁻¹ h⁻¹ at selectivity 99.70%.	[40]

Table 2.6. Summary of some modified TiO₂-based photocatalysts in CO₂ photoreduction (cont.).

Cordierite honeycomb monoliths loaded with N/TiO ₂ and Cu/TiO ₂ nanocatalysts.	- Cu and N shifted band gap energy to include visible region and decreased recombination rate. - Cu/TiO₂ generated CO 14 times higher than N/TiO₂ and 64 times higher than TiO₂ - N/TiO₂ trapped holes and favored CH₄ formation. - Cu/TiO₂ gave negative effect on CH₄ production, but enhanced CO yield. - Cordierite honeycomb support allowed for selective CO₂ photoreduction.	[41]
Au–In modified TiO ₂ nanocatalysts in monolith photoreactor	- Monolith photoreactor displayed effective CO₂ reduction to CO through the RWGS reaction. - CO production rate was 76 times higher compared to the un-doped TiO₂ catalyst. - Quantum efficiency for CO was 0.79%.	[42]

2.4. Reactors in CO₂ Reduction

The photocatalytic yield is influenced by many factors, one of which is the type of photoreactor used and its reaction mode. It is ineffective to study and compare the activity of photocatalysts based on their intrinsic behavior without taking reactor geometries and operating conditions into consideration. Flow reaction systems and batch reaction systems are the two widely studied reaction modes for photocatalytic CO₂ reduction [43].

Batch reactors have been largely reported in the literature, but they possess some key limitations. Since products are left to accumulate in the reactor for a defined period of time, it becomes hard to measure product composition or control the reaction mechanism. This is because the accumulation of products may lead to changes in reactant concentrations via photocatalytic reactions, re-adsorption of intermediates or products, or the occurrence of side reactions like hydrogenation or re-oxidation. In this case, the continuous desorption of products is of utmost importance to reduce such problems [43].

In a continuous flow reactor system, on the other hand, the issues mentioned for batch reactors are not present. However, the yield is the main problem, as the short residence time in these reactors does not allow the reactants and photocatalysts to be contacted properly.

According to the literature, it is possible to obtain a better performance upon optimization of reaction conditions and using effective and strong photocatalysts [43].

The photoreactor for the photocatalytic reduction of CO_2 operates at three main modes: slurry, fixed bed, and membrane photoreactors. Currently, some research has been directed towards monolith photoreactors, which are a type of fixed-bed reactors, due to their multiple channels that provide better contact area. Monolith reactors are especially used in gas-phase systems with H_2 reductant to produce CO [44]. An example of such a photoreactor is present in Figure 2.10a. An enlarged version of the monolith channels is shown in Figure 2.10b.

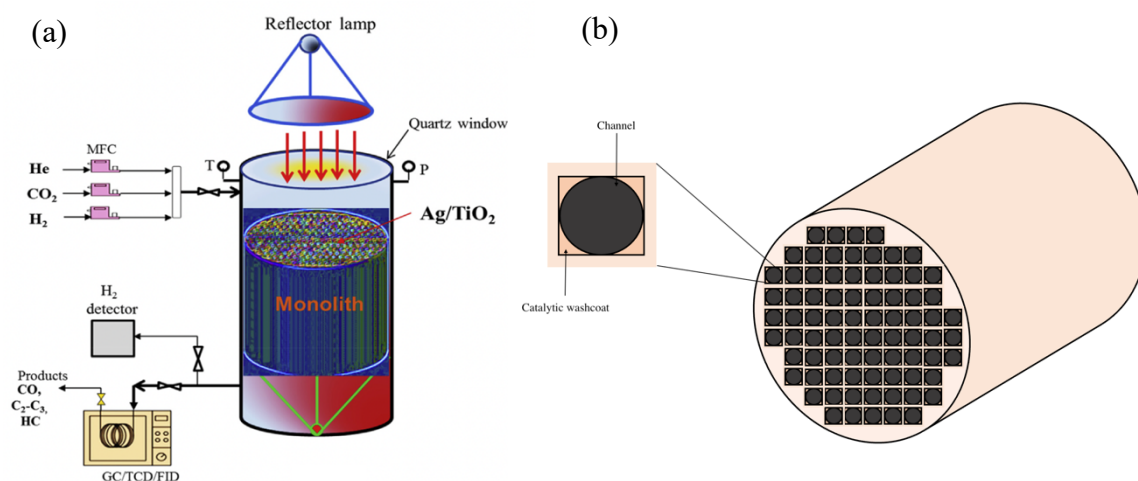


Figure 2.10. (a) Experimental monolith photoreactor, (b) enlarged channels in monolith. Reproduced (a) from ref. [44] with permission from Elsevier copyright, 2017; Adapted (b) from ref [45].

As this process has not yet been industrialized, there is a large number of other preliminary experimental setups available in the literature. These setups are mostly for lab-scale works and need yet to be further enhanced to be used in industrial applications. Examples of such experimental setups are displayed in the next pages (Figures 2.11 – 2.13).

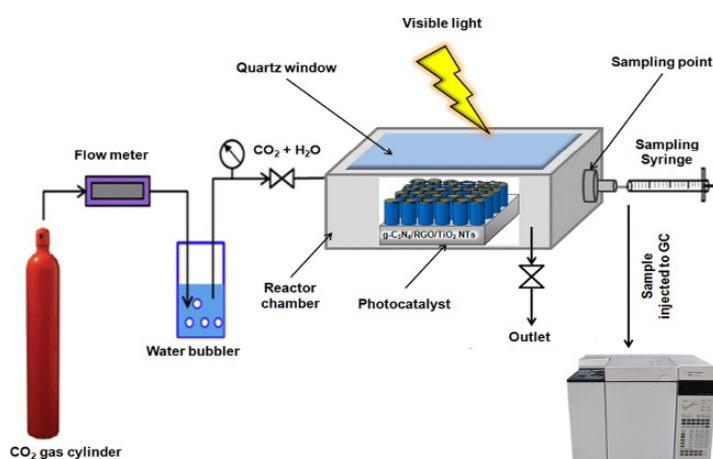


Figure 2.11. Experimental CO₂ photoreduction setup. Reproduced from ref. [46] with permission from Springer Nature copyright, 2021.

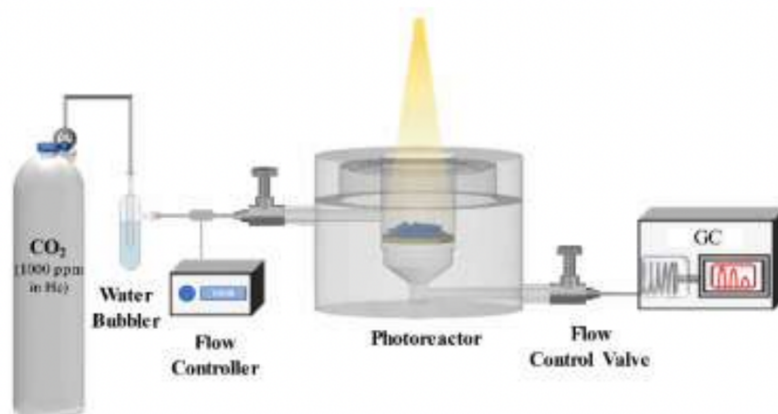


Figure 2.12. Experimental CO₂ photoreduction setup. Reproduced from ref. [47] with permission from Elsevier copyright, 2020.

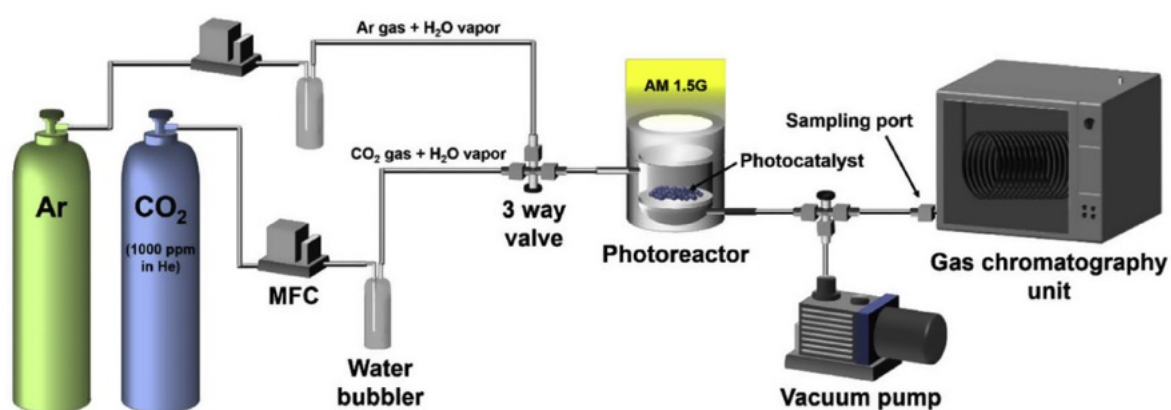


Figure 2.13. Experimental CO₂ photoreduction setup. Reproduced from ref. [43] with permission from MDPI copyright, 2019.

3. EXPERIMENTAL SECTION

3.1. Chemicals Used

The main chemical used in this work is TiO_2 , as all photocatalysts in this work are based on the TiO_2 semiconductor. Table 3.1 displays the kind of TiO_2 chemical used in the experiments, while Tables 3.2 and 3.3 display the precursor chemicals used for obtaining Pt and Cu metals, respectively, for catalyst metal loading. Table 3.4 displays the properties of the urea source used in the deposition precipitation with urea (DPU) photocatalyst preparation method (see section 3.2), while Table 3.5 displays the ionic liquid used.

Table 3.1. TiO_2 chemical used in experiments.

Titanium (IV) Oxide Nano-powder, 21 nm primary particle size (TEM), $\geq 99.5\%$ trace metals basis Aeroxide® P25, Titania, Titanium dioxide	
Formula	TiO_2
CAS Number	13463-67-7
Molecular Weight	79.87 g/mol
Melting Point	1850 °C >350 °C (lit.)
Density	4.26 g/mL at 25 °C (lit.)

Table 3.2. Tetraamineplatinum (II) nitrate chemical used in experiments.

Tetraamineplatinum (II) Nitrate 99.995% trace metals basis Platinum tetraamine dinitrate, Tetraamineplatinum (II) dinitrate, Tetraaminedinitratoplatinum	
Formula	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$
CAS Number	20634-12-2
Molecular Weight	387.21 g/mol
Melting Point	262 °C (dec.) (lit.)

Table 3.3. Copper (II) chloride chemical used in experiments.

Copper (II) Chloride 99.999% trace metals basis Cupric chloride	
Formula	CuCl ₂
CAS Number	7447-39-4
Molecular Weight	134.45 g/mol
Melting Point	620 °C (lit.)
Density	3.386 g/mL at 25 °C (lit.)

Table 3.4. Urea chemical used in experiments.

Urea GR for analysis ACS, Reag.Ph Eur Carbamide, Carbonyl diamide, Diaminomethanone	
Formula	NH ₂ CONH ₂
CAS Number	57-13-6
Molecular Weight	60.06 g/mol
Melting Point	132 – 135 °C (lit.)
Density	1.335 g/mL at 25 °C (lit.)

Table 3.5. Ionic liquid used in experiments.

Ionic Liquid (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ≥ 97.0% (NMR) EMIM BTI, EMIM TFSI, EMIMIm	
Formula	C ₈ H ₁₁ F ₆ N ₃ O ₄ S ₂
CAS Number	174899-82-2
Molecular Weight	391.31 g/mol
Melting Point	≥ – 15 °C (lit.)
Density	/

3.2. Photocatalyst Preparation Procedures

3.2.1. Platinum Loaded TiO_2 Synthesis

To prepare 5 g TiO_2 with 1% Pt particles using the incipient-to-wetness impregnation method, the amount of Pt precursor needed is calculated to be 0.0992418 g. It was found from prior experiments that for this method, the amount of distilled water required to dissolve the metal is double the amount of TiO_2 . This makes sure that the amount of solution is just sufficient to saturate the pores. The preparation procedure taken is thus as follows [48]:

1. Using an ultrasonic mixer, 5 g of TiO_2 nano-powder is mixed while being attached to a vacuum pump for 15 minutes (Figure 3.1).
2. 0.0992418 g of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ is added to 10 mL of distilled water and dissolved using the ultrasonic mixer for 15 minutes.
3. Then, the metal precursor solution is added dropwise onto the TiO_2 using a peristaltic pump (Figure 3.2) and then the mixture is rested under vacuum for 15 – 20 minutes.
4. The sample is then taken to a drying oven to dry overnight (at least 12 hours) at 100 °C.
5. The dry sample is calcined at 673 K for 4 hours in air with a heating rate of 5 °C/min.
6. After calcination, the photocatalyst is weighed and stored (Figure 3.3).

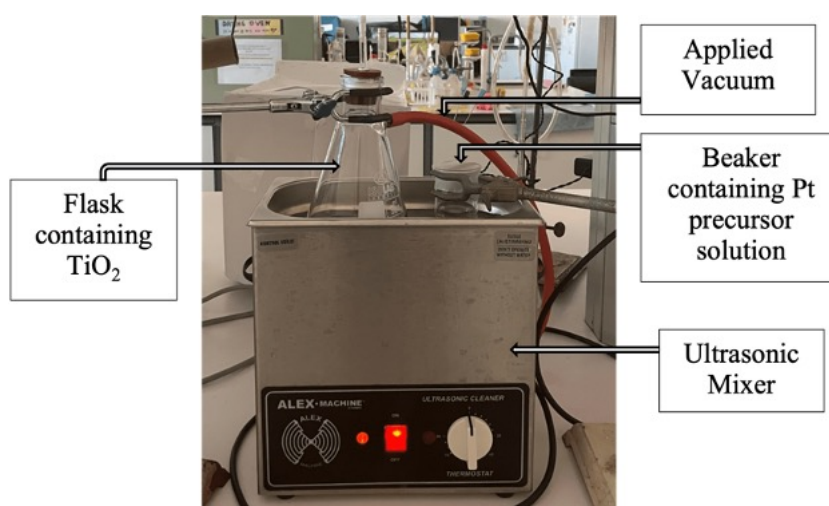


Figure 3.1. Separate ultrasonic mixing of TiO_2 and Pt solution.

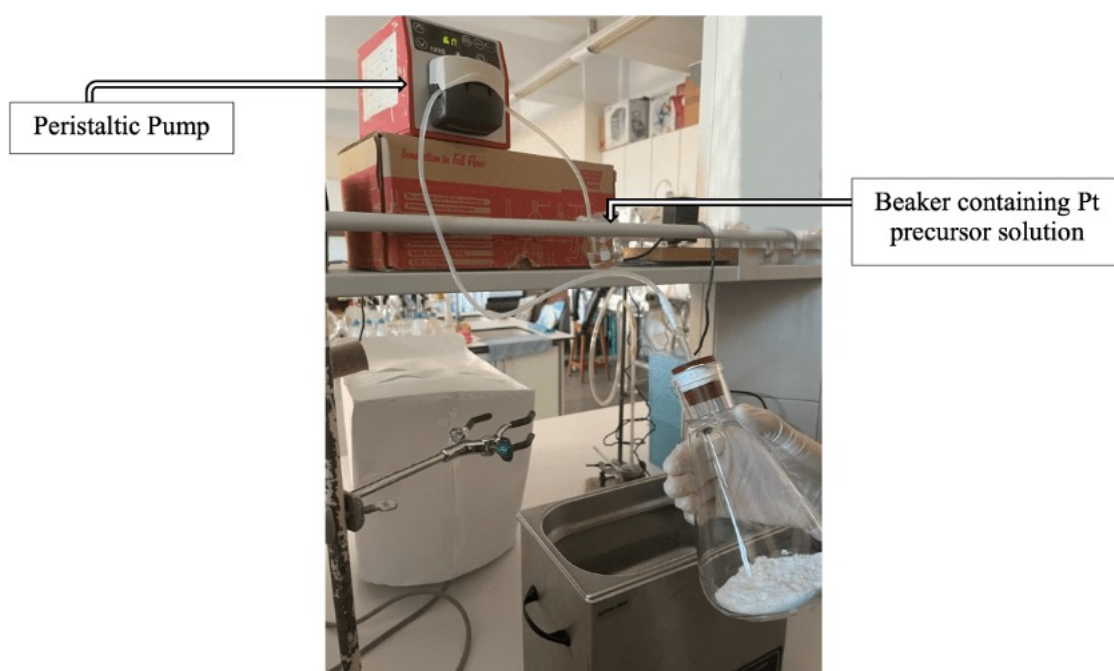


Figure 3.2. Dropwise addition of Pt.

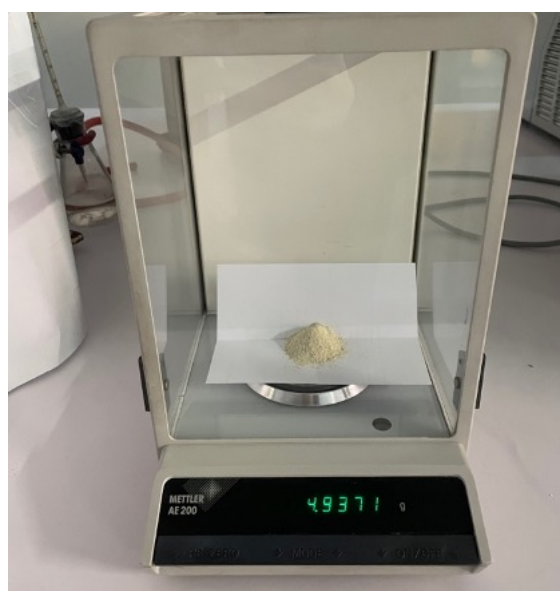


Figure 3.3. Weighing Pt/TiO₂ photocatalyst after calcination.

3.2.2. Copper Loaded TiO₂ Synthesis

To prepare 5 g of 1% Cu/TiO₂ photocatalyst, the Deposition Precipitation with Urea (DPU) technique is used. The steps are as follows [48]:

1. 5 g of TiO₂ nano-powder is added to 100 mL distilled water to form Mixture 1.
2. 0.05 g of CuCl₂ is added to 24 mL distilled water to form Mixture 2.
3. 8.5766 g of urea is added to 216 mL distilled water to form Mixture 3.
4. Using the ultrasonic mixer, Mixture 1 and Mixture 2 are stirred for 1 hour under dark conditions (Figure 3.4a).
5. Then, Mixture 2 is deposited onto Mixture 1 in a dropwise fashion using a pipet.
6. The solution is stirred for another hour under dark conditions (Figure 3.4b).
7. Mixture 3 containing urea is added to the suspension and stirred for 4 hours at 80 °C.
8. The (Cu/TiO₂+Distilled water+Urea) solution is rested under dark conditions for 1 day.
9. After 24 hours, the catalyst is divided into four samples, which are washed and centrifuged under dark conditions several times to get rid of the urea. After each washing, the pH of the sample is checked.
10. When the pH of all four samples drop to around 7.0, the samples are put on petri dishes and placed in the drying oven at 100 °C to dry overnight.
11. The dry sample is calcined at 673 K for 4 hours in air with a heating rate of 5 °C/min.
12. After calcination, the photocatalyst is weighed and stored.

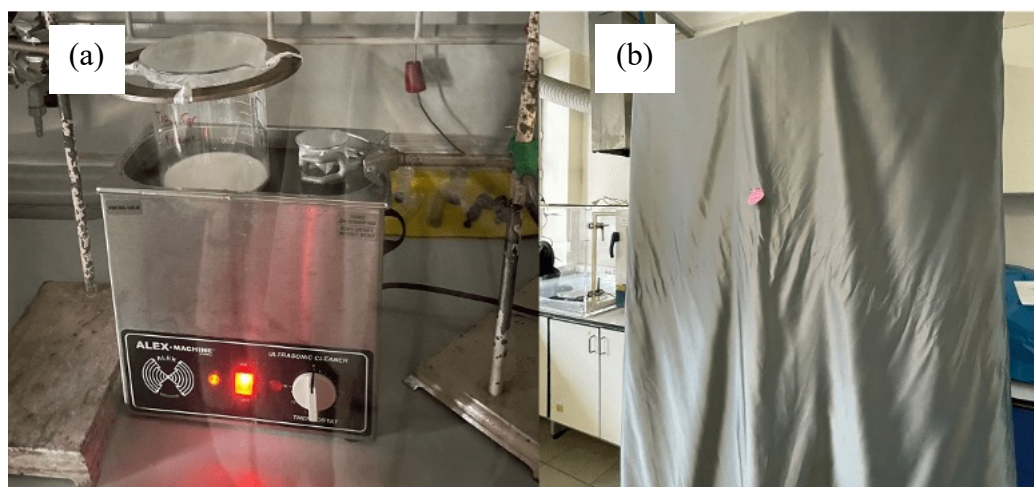


Figure 3.4. (a) Stirring mixture 1 and mixture 2, (b) procedure under dark conditions.

3.2.3. Ionic Liquid Coating of Platinum Loaded TiO_2

For every 1 g of 1% Pt/TiO_2 photocatalyst, 200 mg of ionic liquid (IL) and 4 g of acetone is required. The coating procedure is as follows [48]:

1. The photocatalyst to be coated, Pt/TiO_2 , is placed in a small flask in the glovebox.
2. While it is being weighed, 200 mg of IL is added.
3. Then, 4 g of acetone is added to the mixture.
4. Using a magnetic stirrer kept inside the glovebox, the mixture is stirred at 225 rpm for 1 hr. (Figure 3.5a).
5. The sample is then placed in the vacuum oven at 333 K and 0.5 bar for 7 hours (Figure 3.5b).
6. The coated photocatalyst is weighed and stored.

3.2.4. Ionic Liquid Coating of Copper Loaded TiO_2

The same process mentioned for coating 1% Pt/TiO_2 is applied to 1% Cu/TiO_2 .

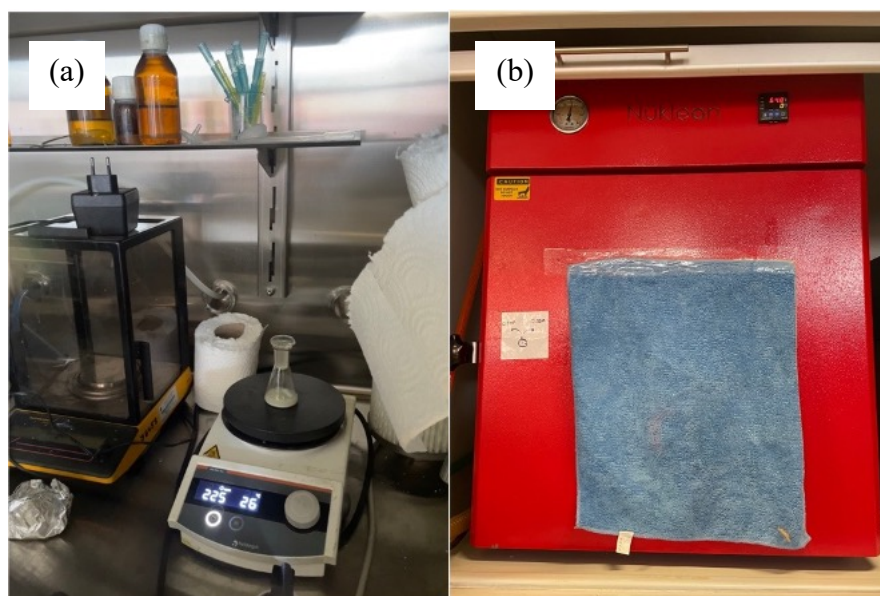


Figure 3.5. (a) Stirring ionic liquid condition in glovebox. (b) drying under vacuum.

3.2.5. Bimetallic Copper/Platinum Loaded TiO₂ Synthesis

To prepare 0.1 g of bimetallic 0.35%Pt-1%Cu/TiO₂ photocatalyst, the photo-deposition method is utilized. First, 0.35%Pt/TiO₂ is prepared, and then the same procedure is applied again for depositing 1%Cu on the prepared photocatalyst. The procedure is as follows [34]:

1. 0.1 g of TiO₂ nano-powder is added to 20 mL DI water and 5 mL CH₃OH.
2. Around 0.0007 g of [Pt (NH₃)₄](NO₃)₂ (for 0.35 % Pt) is added to the above mixture and stirred for 1 hour in a closed system in the dark (Figure 3.6a).
3. The suspension is then illuminated under AM 1.5 for 2 h with mild stirring.
4. The sample is then centrifuged and washed repeatedly with DI water.
5. The sample is dried at 90 °C in a vacuum oven (0.5 bar) for 12 h.
6. The prepared 0.35 % Pt/TiO₂ photocatalyst (Figure 3.7a) is weighed and then added again to 20 mL DI water and 5 mL CH₃OH to deposit the Cu metal.
7. Around 0.002 g of CuCl₂ (for 1 % Cu) is added to the above mixture and stirred for 1 hour in a closed system in the dark.
8. The suspension is then illuminated under AM 1.5 for 2 h with mild stirring.
9. The sample is then centrifuged and washed repeatedly with DI water.
10. The sample is dried at 90 °C in a vacuum oven (0.5 bar) for 12 h.
11. The prepared 0.35 % Pt- 1% Cu/TiO₂ photocatalyst (Figure 3.7b) is weighed.
12. The prepared photocatalyst samples are mixed well in a crucible (Figure 3.8).

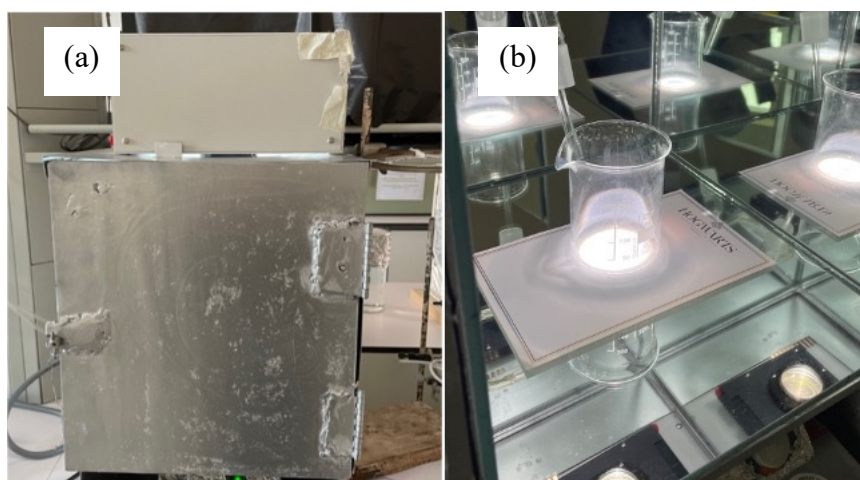


Figure 3.6. (a) Closed system for stirring and illumination, (b) AM1.5 light output.

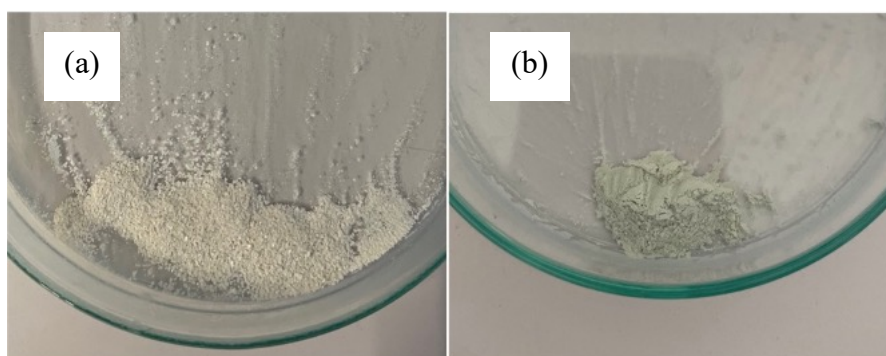


Figure 3.7. (a) 0.35%Pt/TiO₂, (b) 0.35%Pt-1%Cu/TiO₂.

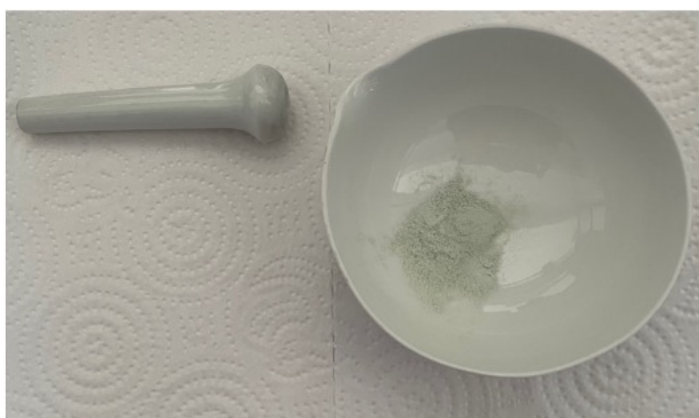


Figure 3.8. Mixing the prepared 0.35%Pt-1%Cu/TiO₂ samples.

3.2.6. Ionic Liquid Coating of Bimetallic Copper/Platinum Loaded TiO₂

The same process for IL coating of 1% Pt/TiO₂ and 1% Cu/TiO₂ is applied to 0.35%Pt-1%Cu/TiO₂.

3.3. Equipment and System Setup

3.3.1. Equipment Used

The equipment used for photocatalyst preparation are summarized in Table 3.6, while the equipment used in the process of CO₂ photocatalytic reduction are listed in Table 3.7.

Table 3.6. Equipment used for photocatalyst synthesis.

Ultrasonic Cleaner (Mixer)		
Product Code	AXUY-04	
Company	Alex Machine	
Peristaltic Pump		
Product Code	013.5000.00A	
Company	Watson Marlow	
Drying Oven		
Product Code	M420	
Company	Elektro-mag	
Calcination Oven		
Product Code	PC109	
Company	GEMO	
pH Meter		
Product Code	pH 3210 Set 3 (330i)	
Company	WTW	
Centrifuge		
Product Code	NF 400	
Company	Nuve	

Table 3.6. Equipment used for photocatalyst synthesis (cont.).

Glovebox		
Product Code	VGB-6	
Company	Siemens	
Vacuum Oven		
Product Code	NVE Series	
Company	Nukleon	

Table 3.7. Equipment used in the process system.

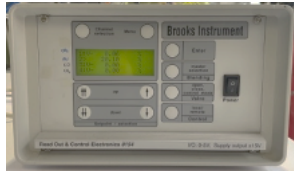
Mass Flow Controller (MFC)		
Product Code	5850E	
Company	Brooks Instrument	
Read Out and Control Electronics (Set Point Controller)		
Product Code	0154	
Company	Brooks Instrument	
Gas Chromatograph		
Product Code	GC-2014	
Company	Shimazdu	
Magnetic Stirring Hotplate		
Product Code	MR 3001 K	
Company	Heidolph	
Heating Cables		
Product Code	SDD20 220V 80W	
Company	Sedes Group	

Table 3.7. Equipment used in the process system (cont.).

Temperature Controller		
Product Code	XT111C	
Company	Dixell	
Solar Simulator (DC Xenon Arc Lamp)		
Product Code	U.S. Patent 8116017	
Company	ABET Technologies	
Solar Simulator (UV-Vis)		
Product Code	SF300-C	
Company	ScienceTech	
UV Lamp		
Product Code	HPI-T Plus 250W/645	
Company	Philips	

3.3.2. Calibrations

The photocatalytic CO₂ reduction system presented in this work is constructed from scratch. Therefore, the mass flow controllers (MFCs) and the Gas Chromatograph (GC) needed calibration before operation. The GC calibrations were done for all the gases expected to appear in the process (i.e., both reactants and products). Thus, the GC gas calibrations were performed for CO₂, CO, CH₄, H₂, O₂, and N₂ (N₂ indicates the amount of air present in the system). The GC column utilizes Ar as the carrier gas, which is also the same as the inert carrier gas used in the system. To be able to inject all the gases to the GC to perform the calibrations, MFCs were required for each gas as well. So, MFC calibrations had to be performed for CO₂, CO, CH₄, H₂, O₂, and Ar. The MFC used to inject N₂ to the GC did not need to be calibrated because it had been used and calibrated for N₂ already.

3.3.2.1. MFC Calibrations. The MFCs used for the gases are selected based on their specifications, as each MFC has a specific flow range along with a specific gas for which it is made. Gases with similar molecular weights can be alternatively used if needed. Figure 3.9 displays the calibration curve and correlation for each gas. The desired flowrate for reactants can be easily achieved by selecting the corresponding set point in the Brooks Instrument Read-Out Controller.

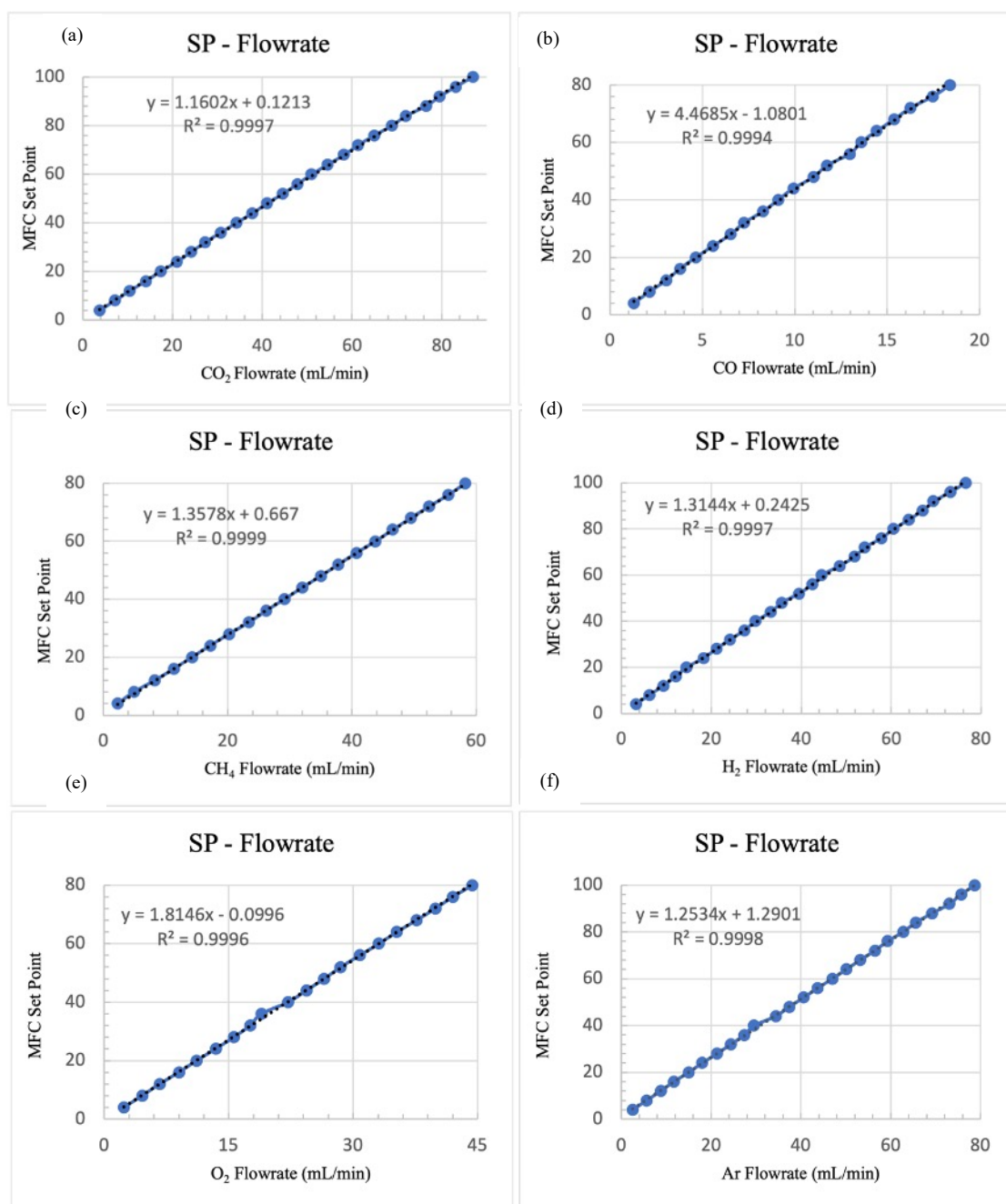


Figure 3.9. MFC calibrations of (a) CO₂, (b) CO, (c) CH₄, (d) H₂, (e) O₂, (f) Ar flows.

3.3.2.2. GC Calibration. After calibrating the MFC's for each gas, all the gases were injected into the GC at several flowrates corresponding to different concentrations to perform the GC calibration. After testing different flowrates and concentrations for each gas, the data summarized in Table 3.8 was obtained.

Table 3.8. GC gas calibrations.

Gas	H ₂	O ₂	N ₂	CO	CH ₄	CO ₂
Column Temperature (°C)	30	46.5	47.2	56	97.4	138
Time (min)	2.18	6.31	6.45	8.18	17.51	25.65

Table 3.8 shows the times and temperatures at which each gas was detected by the GC in the form of a peak. Inputting the data into the GC solution program allowed for the assigning and recognition of the peaks to correspond to their specific gases upon detection. The GC can indicate the identity of the gases obtained from the process and their concentration values from the area of their peaks. Figures 3.10–3.15 display the obtained calibration curve and correlation for each gas.

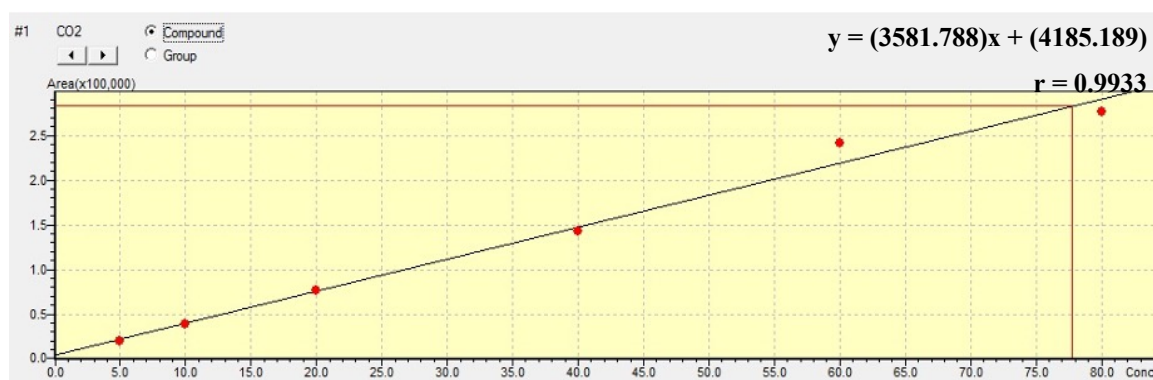


Figure 3.10. GC calibration curve for CO₂.

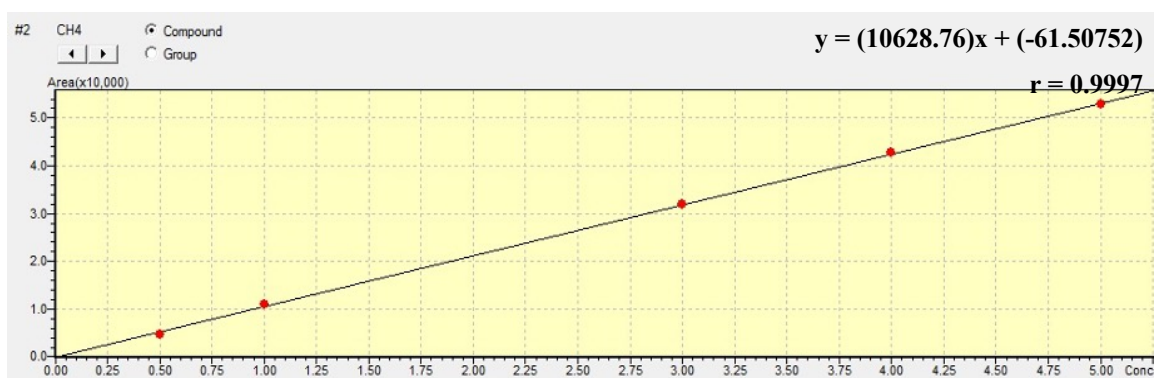
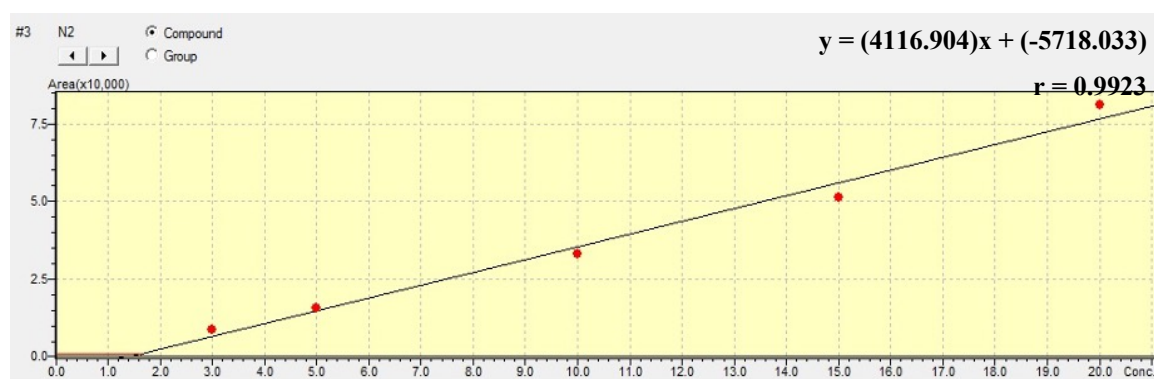
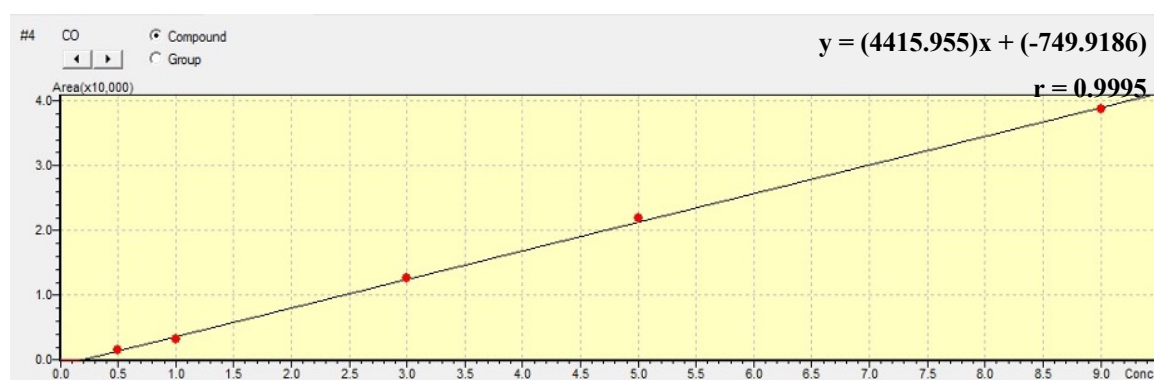
Figure 3.11. GC calibration curve for CH₄.Figure 3.12. GC calibration curve for N₂.

Figure 3.13. GC calibration curve for CO.

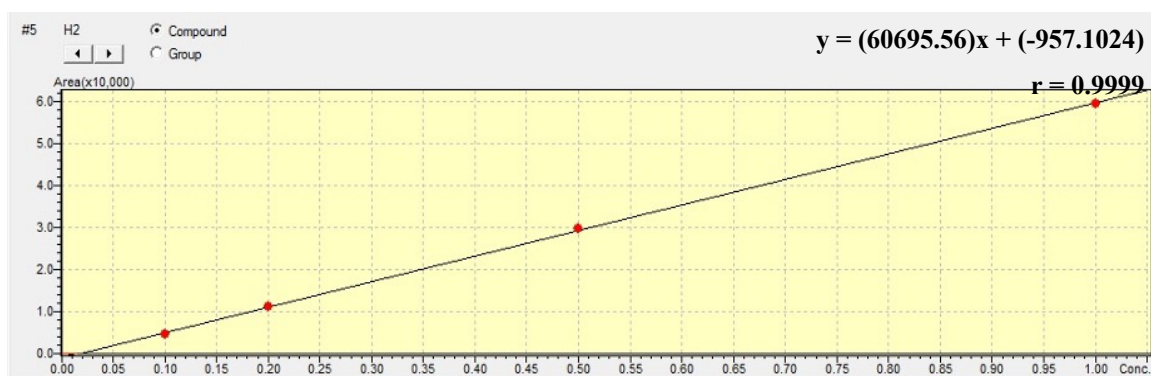


Figure 3.14. GC calibration curve for H₂.

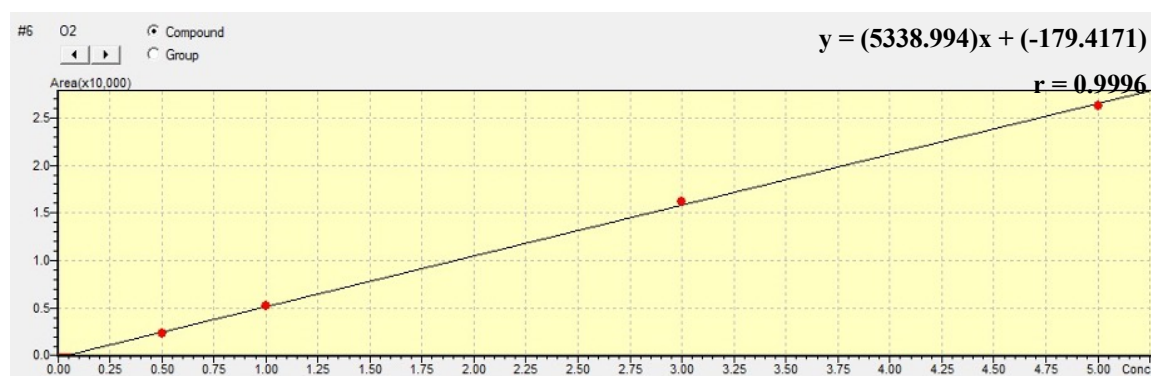


Figure 3.15. GC calibration curve for O₂.

3.3.3. System Design

The process designed for the photocatalytic reduction of CO₂ consists of the following main units: 1) Two Ar Pressurized Tubes (GC carrier gas + system carrier gas), 2) One CO₂ Pressurized Tube (reactant), 3) Water Bubbler (WB), 4) Photoreactor, 5) Light Source, 6) Water Trap, 7) Gas Chromatograph (GC), and 8) Display Screen (GC Data Analysis). Figure 3.16 displays a simple block flow diagram of the process.

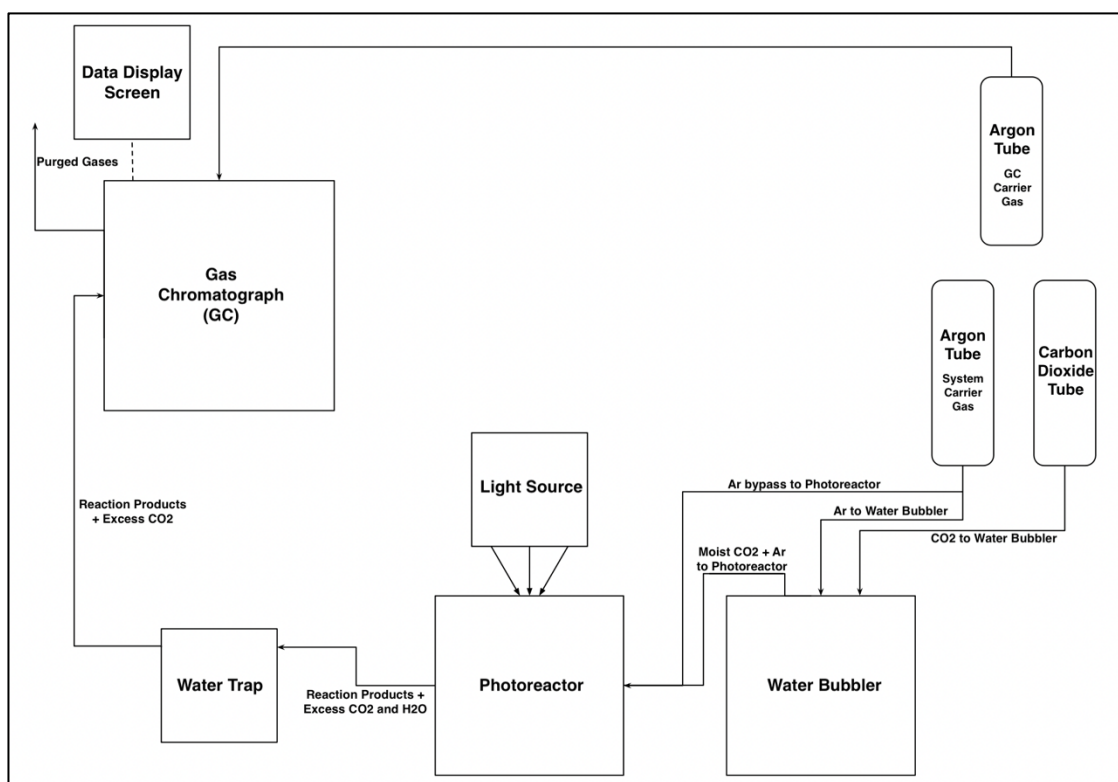


Figure 3.16. Block flow diagram (BFD) of the process.

The process starts with CO₂ and Ar (as carrier gas) flowing through their separate MFCs at the desired entered flowrate. For Ar, it passes through a two-way valve (on/off) and flows towards another three-way valve where it separates into a pipe going into the water bubbler, and another pipe heading to the photoreactor directly. This Ar bypass line is installed to be able to inject Ar by itself into the photoreactor for cleaning and/or to purge any air left in the reactor before operation. At the water bubbler exit, another three-way valve is placed to either take the Ar bypass line or the gases leaving the water bubbler to the photoreactor (Figure 3.16). Figure 3.17 shows the two three-way valves implemented for this purpose. When the arrow points towards “W” on both sides, normal operation with Ar going into the water bubbler occurs. When the arrow points the opposite way, Ar is delivered to the photoreactor directly without anything coming out of the water bubbler.

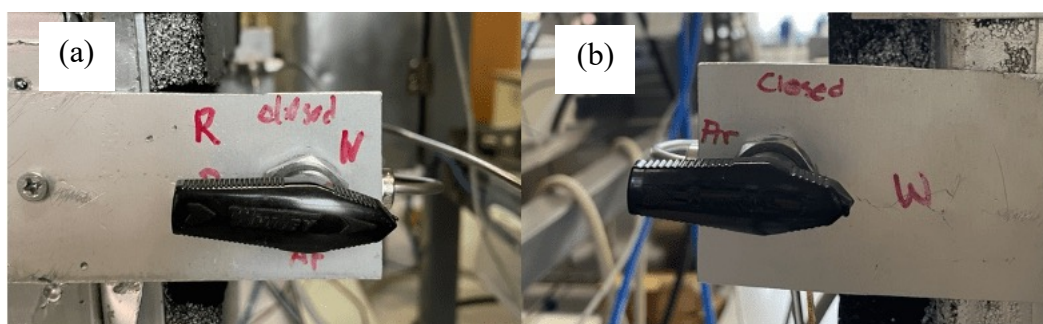


Figure 3.17. (a) Three-way valve before WB, (b) three-way valve after WB.

The CO_2 exiting the pressurized tube also passes through a two-way valve (on/off). After leaving its MFC, it is either directed into a line heading directly to the water bubbler or into another line for purging (utilized in CO_2 MFC calibration). Both the Ar and CO_2 water bubbler inlet lines are extended underneath the water surface to create bubbles. The gas exit line is kept slightly above the water surface, from which the moist CO_2 and Ar gas can then leave the water bubbler through the three-way valve shown in Figure 3.17b and head to the photoreactor.

Three designs for the water bubbler are experimented with. In the first design, a flask is used with a red rubber head sealing it from the top. Holes just big enough for the lines to pass through are created in the head. A total of four small holes, one for inlet Ar, one for inlet CO_2 , one for gas exit (moist CO_2 + Ar), and one for a thermocouple, are punctured. The rubber head is securely sealed to avoid any air leakage into the system. The thermocouple, attached to a temperature controller, is used to measure the temperature of the water to be able to calculate its vapor pressure and the corresponding $\text{H}_2\text{O}/\text{CO}_2$ ratio. In this first design, the water bubbler is placed on top of a hotplate that provides the heating needed to reach the desired H_2O temperature. Figure 3.18 displays the first experimented water bubbler design.

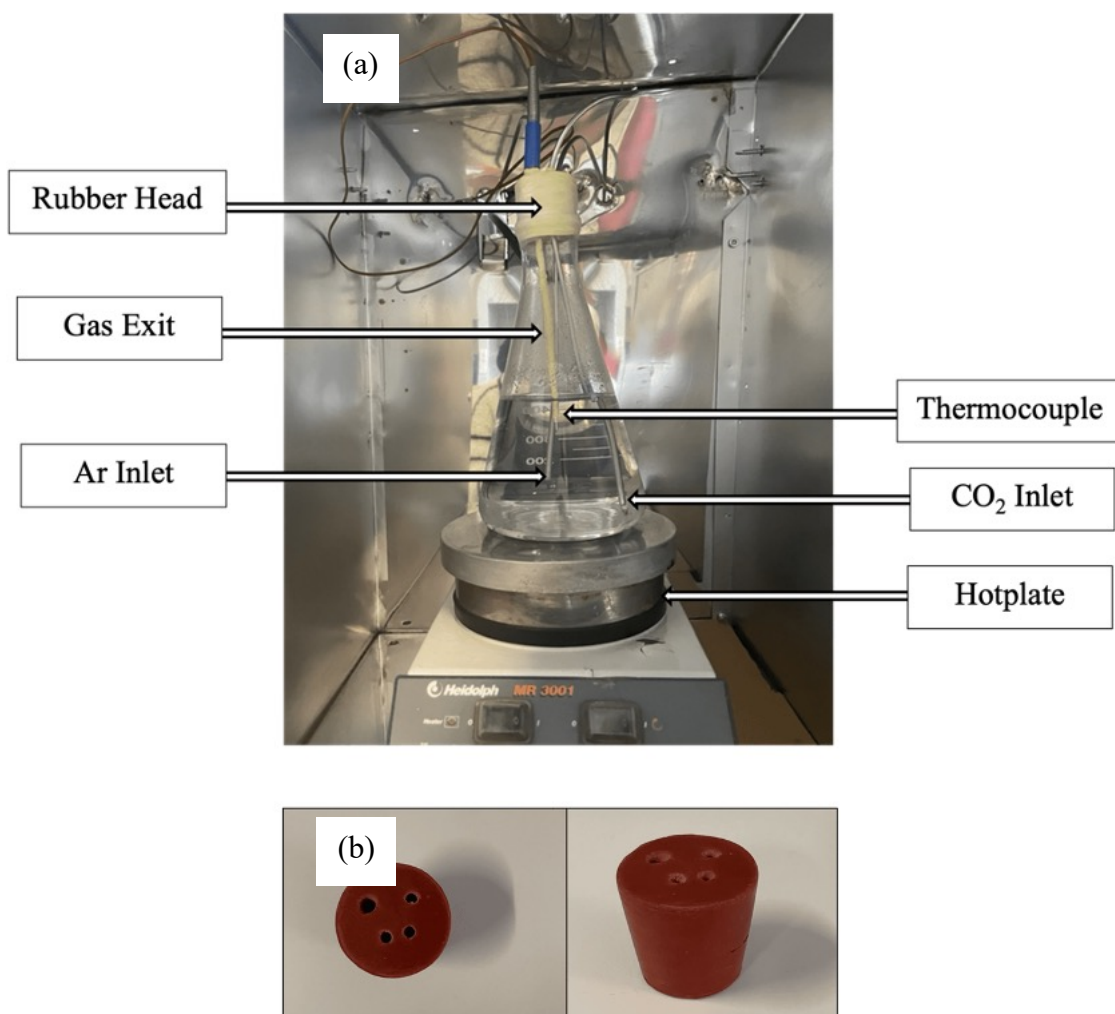


Figure 3.18. (a) First water bubbler, (b) punctured red rubber head.

In the second water bubbler design, the flask is replaced by a cylindrical glass container and the rubber head is replaced by a glass head composed of glass inlets and outlets, as depicted in Figure 3.19. Plastic pipes are also used instead, as the stainless-steel ones cannot be connected to the glass inlets/exit.

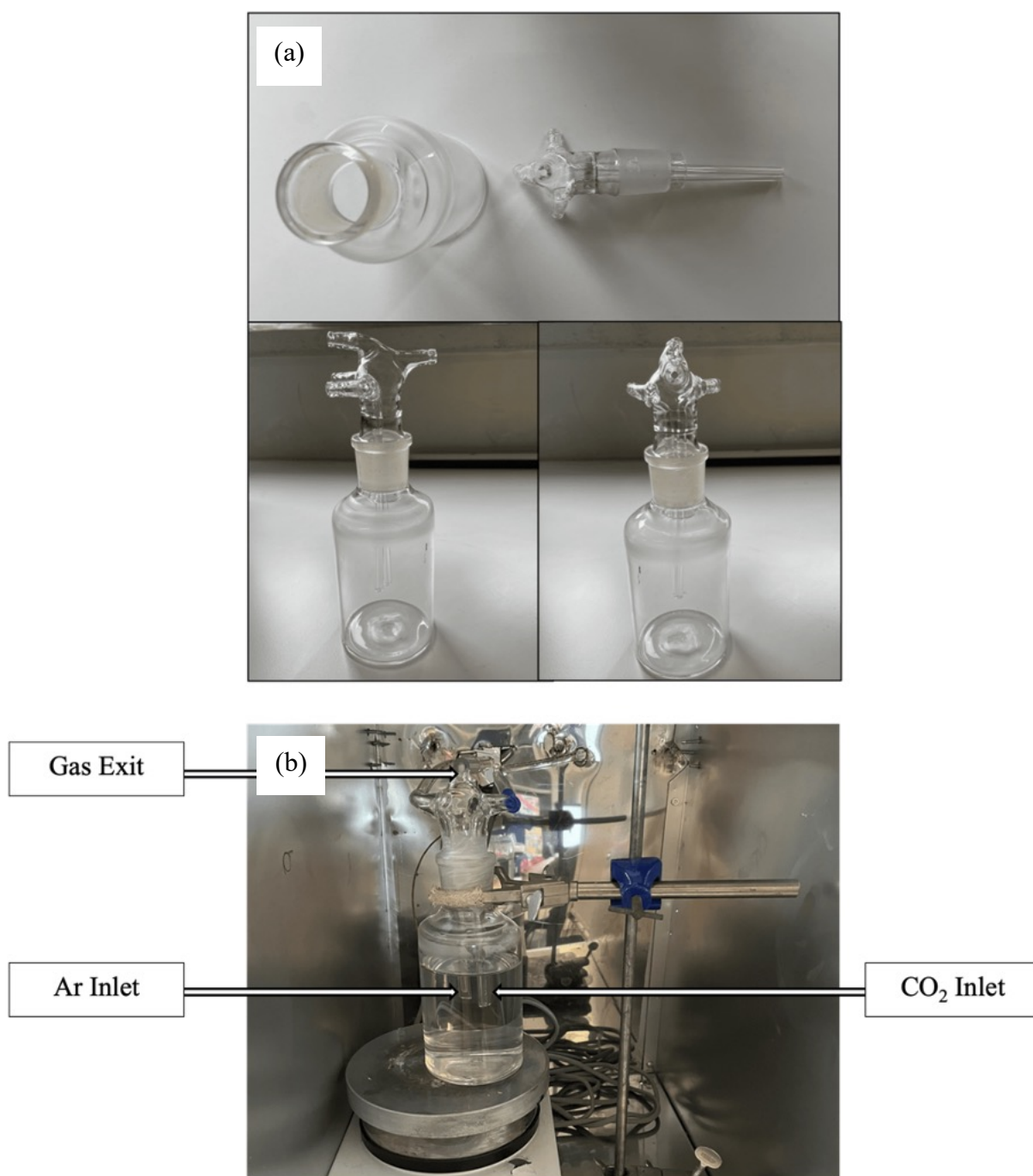


Figure 3.19. (a) Glass head and glass container, (b) second water bubbler.

In the second design, the container is also placed on top of a hotplate for heating. However, condensation at the gas exit was noticed after operation, limiting the amount of water going into the photoreactor. Thus, heating cables were wrapped around the water bubbler to avoid water accumulation at the exit and along the inner glass surface. This is depicted in Figure 3.20.

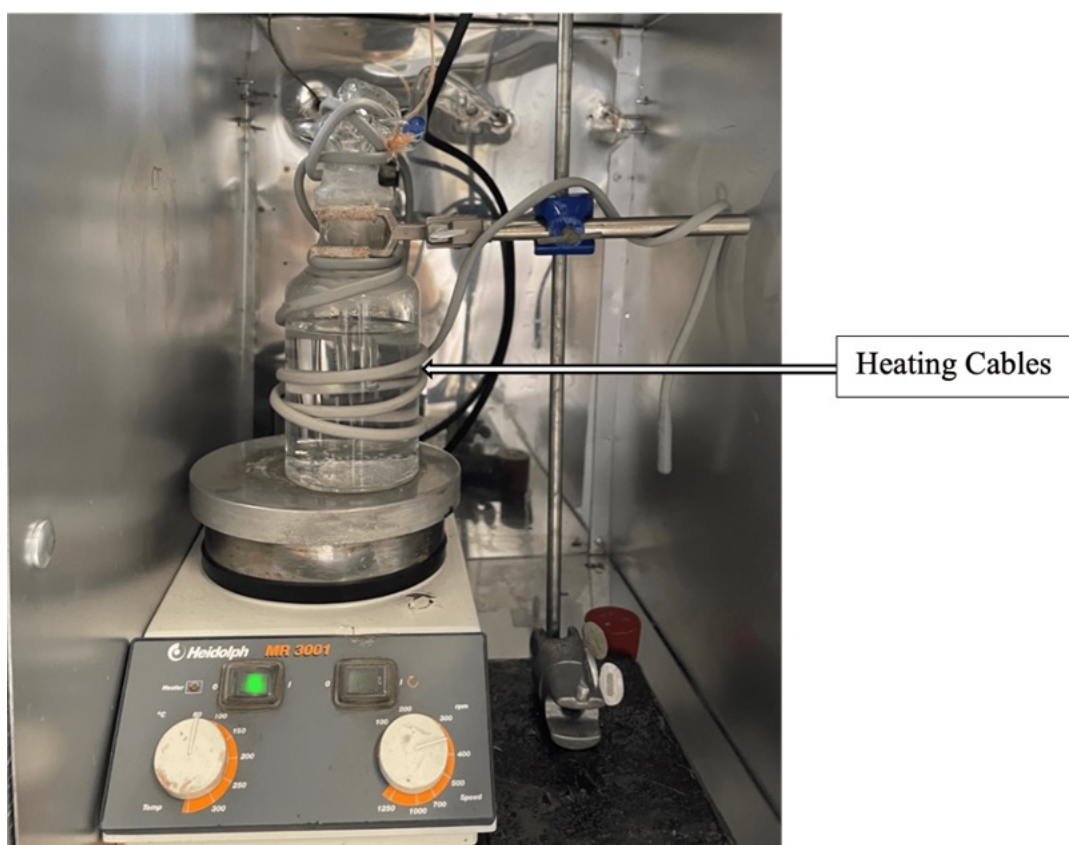


Figure 3.20. Second water bubbler with heating cables.

The third water bubbler design tested consisted of the same cylindrical container as the second design but with another punctured black rubber head instead of the glass head. The black rubber head is smaller than the red one and thus fits the cylindrical container easily. Likewise, the black rubber head is also punctured to give four holes. However, instead of using the hotplate for heating, this third water bubbler is effectively surrounded by heating cables to yield the desired heating, as shown in Figure 3.21.

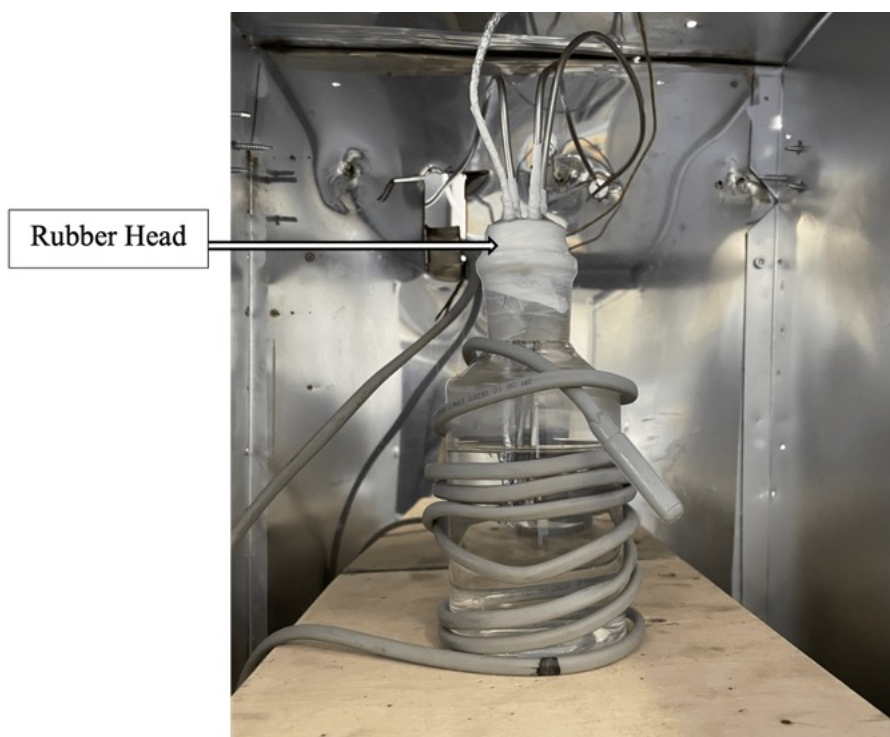


Figure 3.21. Third water bubbler

Table 3.9 presents the type of water bubbler used in each of the undertaken experiments. The experiments are summarized in section 3.4 and discussed in chapter 4.

Table 3.9. Water bubbler design in each experiment.

Type of Water Bubbler Used	Experiments
WB Design 1	1 – 13
WB Design 2	14 – 16 (+ Water Splitting Experiment 1)
WB Design 3	17 – 42 (+ Water Splitting Experiment 2, 3)

After leaving the water bubbler, the exit gas (moist CO_2 + Ar), reaches the photoreactor inlet. The photoreactor used is made of glass to allow light to pass through upon irradiation. The photocatalyst is placed inside the photoreactor and the gases are allowed to pass through. Different glass photoreactor geometries are designed and tested. The first design consisted of a tubular glass reactor with an arched thick bulge in the middle, shown in Figure 3.22.

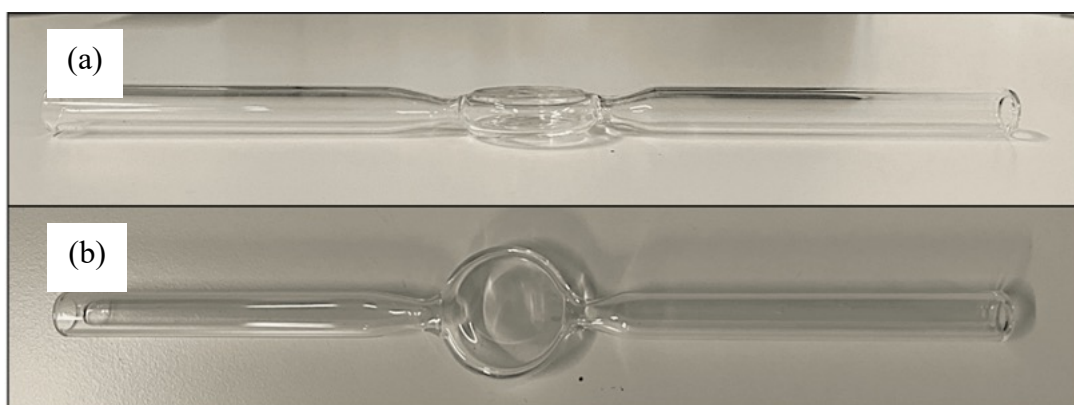


Figure 3.22. Top and side view of first photoreactor design.

The bulge of the tubular reactor is filled with the prepared photocatalyst, which is fixed in place by glass wool on both ends (Figure 3.24 on the next page). To avoid wasting photocatalyst, this design is further improved by compressing it from the middle to create another tubular reactor design with a thinner bulge, as shown in Figure 3.23.

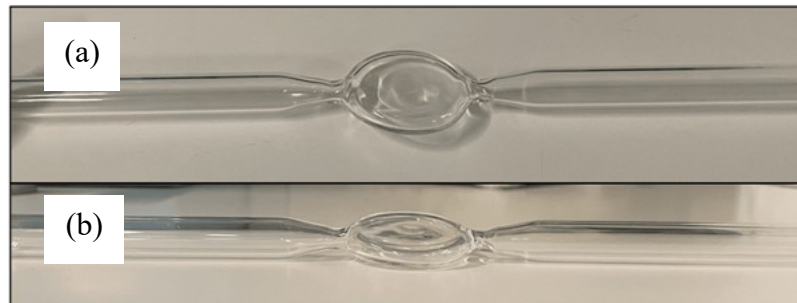


Figure 3.23. Top and side view of second photoreactor design.

Figure 3.24 shows the two mentioned designs after being filled with photocatalyst and attached to the inlet and exit lines by stainless steel connectors.

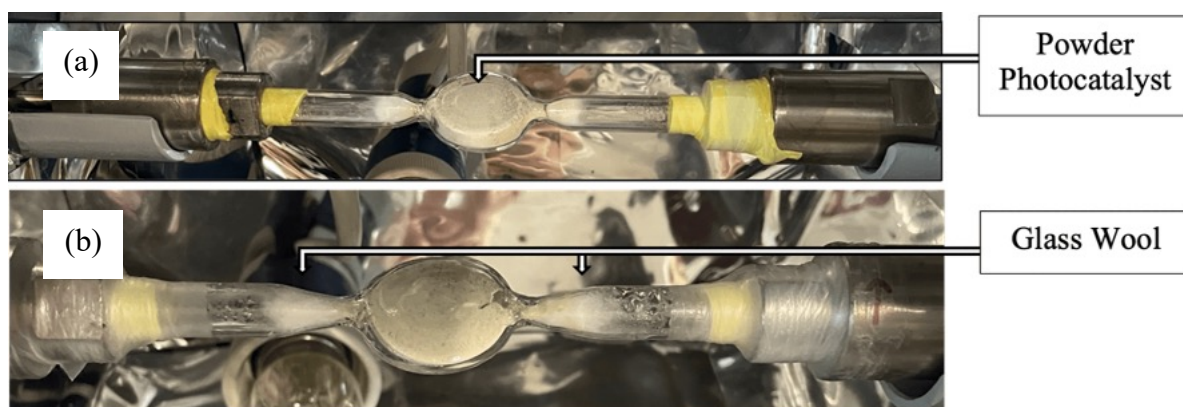


Figure 3.24. (a) First (thick) and (b) second (thin) photoreactors filled with photocatalyst.

The next photoreactor used in the experiments is composed of a glass head attached to a round-shaped glass container design (balloon photoreactor). The glass head has an inlet glass channel going down and an outlet at the top, as displayed below in Figure 3.25.

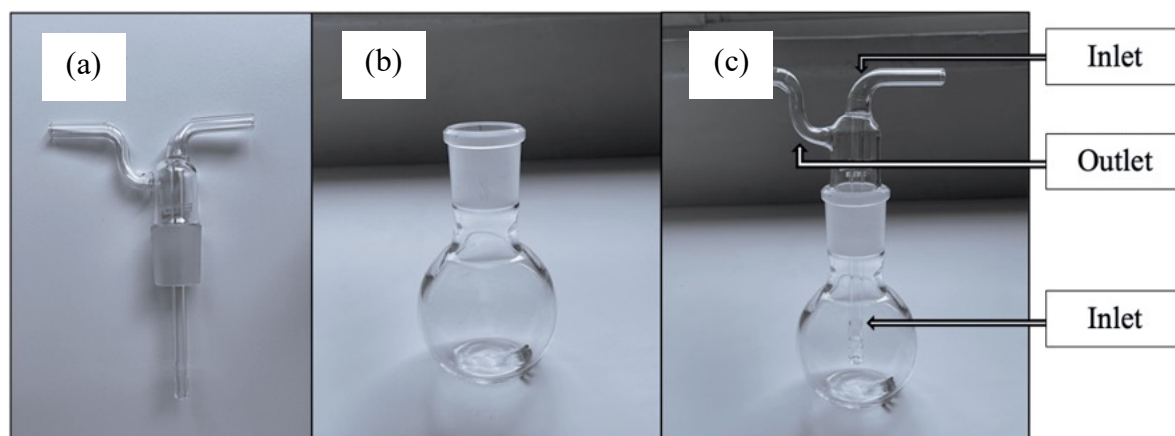


Figure 3.25. Third photoreactor design.

The photocatalyst is placed on the circular flat surface at the bottom of the photoreactor just below the inner glass channel exit. The glass head inlet and outlet are connected to the system via plastic pipes, which were heated to be sealed onto the glass surface (Figure 3.36).

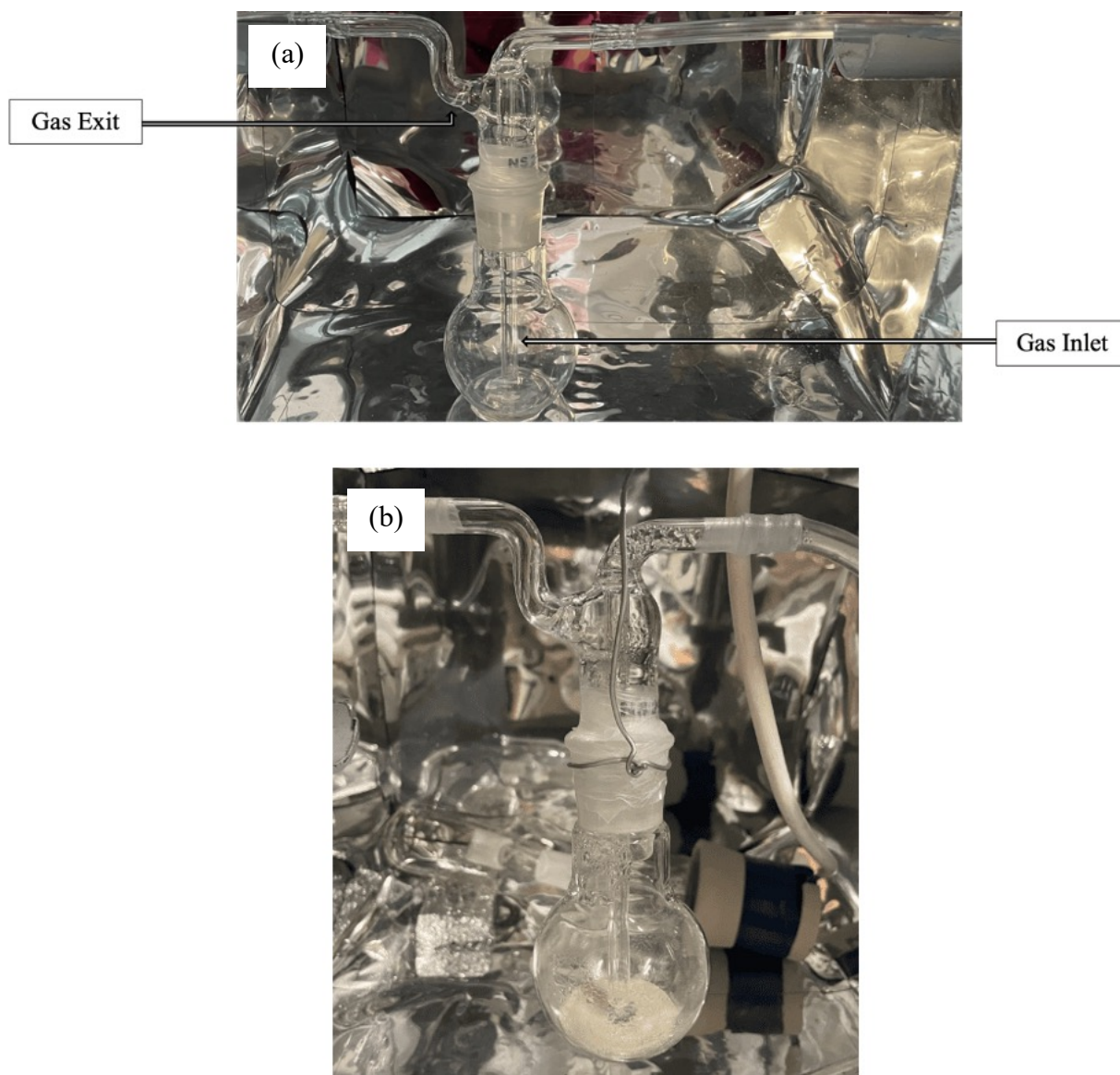


Figure 3.26. (a) Third (balloon) photoreactor design, (b) photoreactor filled with photocatalyst.

After leaving the photoreactor, the product gases pass through a water trap before heading to the Gas Chromatograph (GC) device. Since this work is focused on gas-phase CO_2 photocatalytic reduction, the water trap condenses any excess H_2O , as well as other condensable products such as methanol, etc., before reaching the GC. Two types of water traps are utilized, which are shown in Figure 3.27a.

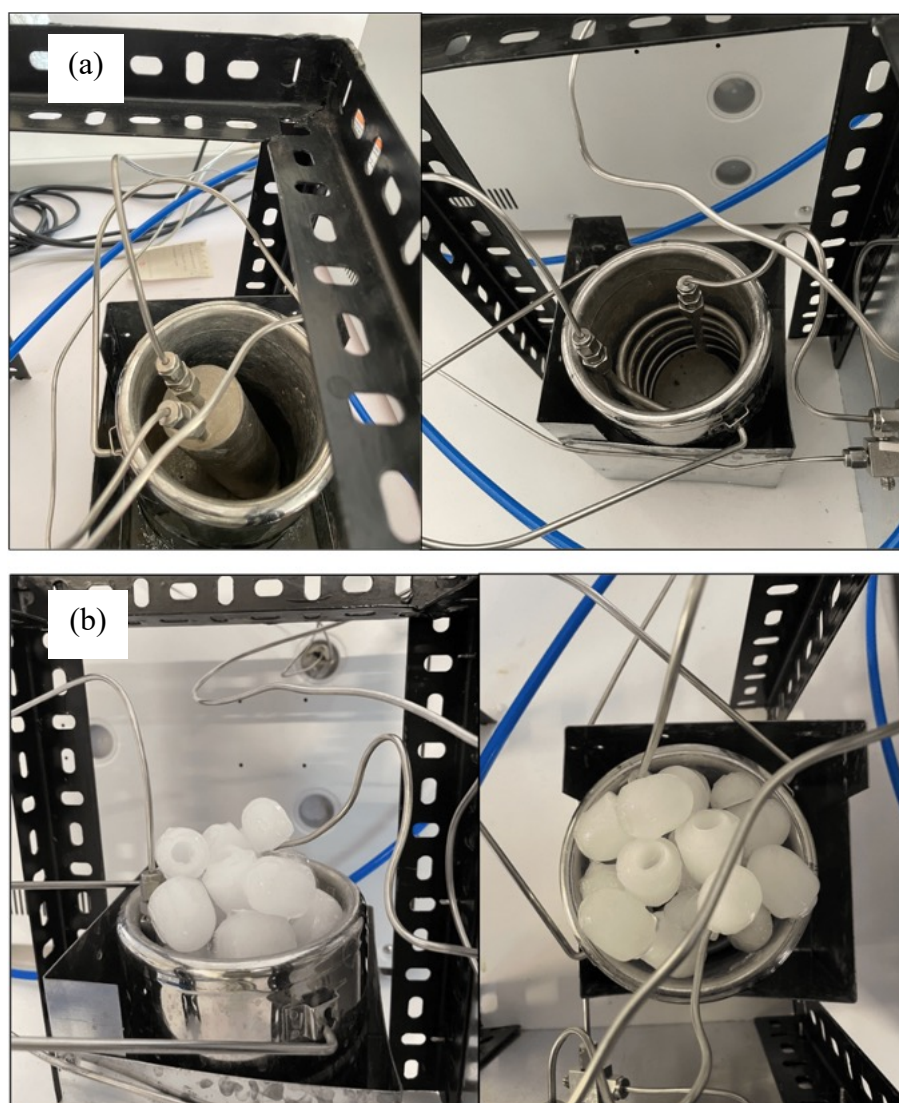


Figure 3.27. (a) Water trap types used, (b) water traps filled with ice.

The gas products are detected by the Gas Chromatograph and then analyzed by the GC Solution program based on the calibrations previously performed (subsection 3.4.2.). The gases are then purged safely. Figure 3.28 displays the key units of the system in the laboratory. Both the water bubbler and photoreactor are placed inside chambers, which were specifically made as a safety precaution and to effectively perform photocatalysis in the reactor chamber without outside interference. The reactor chamber's inner walls are also covered with adhesive mirrors to increase the effectivity of the process, as displayed in Figure 3.29.

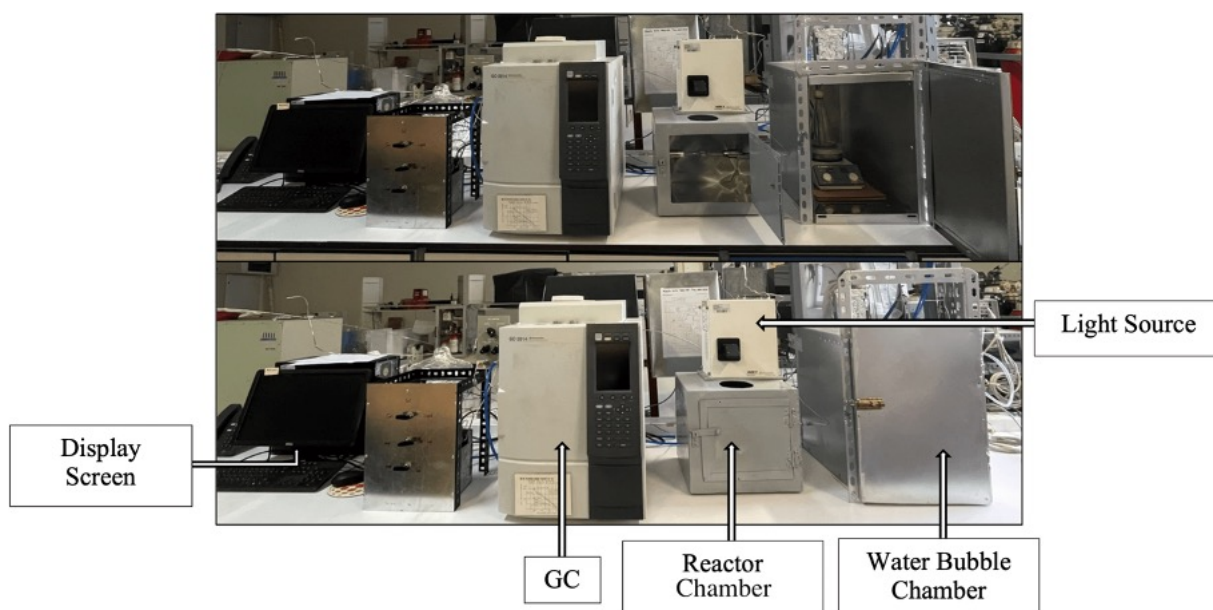


Figure 3.28. Key units of the system.

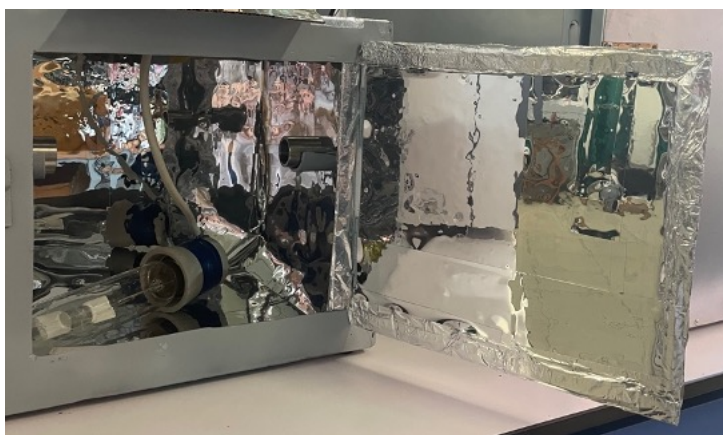


Figure 3.29. Reactor chamber with adhesive mirrors.

3.3.4. Light Sources Used

Two types of light sources are utilized throughout the conducted experiments.

3.3.4.1. UV Light. To get a better idea about the identity of the products, UV light is used to give the strong illumination required to produce and observe even the smallest amounts of products. However, continuous fanning is needed to avoid excess heating in the reactor

chamber. The UV lamp is placed under the glass photoreactors in the reactor chamber as shown in Figure 3.30.

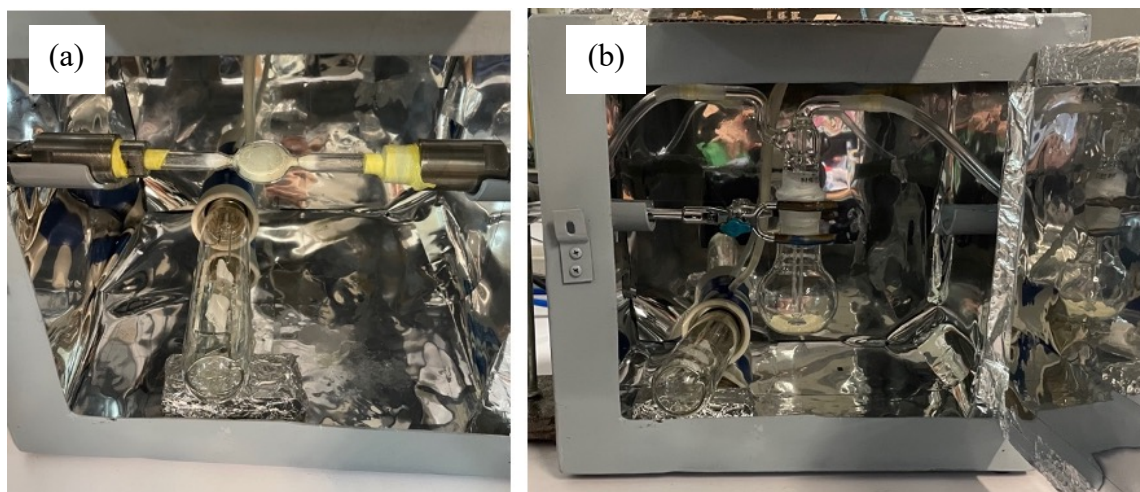


Figure 3.30. UV lamp used with (a) first photoreactor, and (b) third photoreactor.

3.3.4.2. UV-Visible Light (Solar Simulators). Since the aim of the photocatalytic CO₂ reduction process is mimicking photosynthesis, it is important to also test a light that has both UV and visible light wavelengths, as that best simulates sunlight. Two xenon arc lamp devices are experimented with, one with 150 W (UV-Vis1) and the other with 300 W (UV-Vis2). The 150 W solar simulator is from ABET Technologies. This device can produce a 1 Sun output (AM1.5) up to a 3.5 cm diameter field, and it can be focused or defocused depending on the area of interest. Thus, the exposed area of the tubular photoreactors were designed accordingly (Figure 3.31).

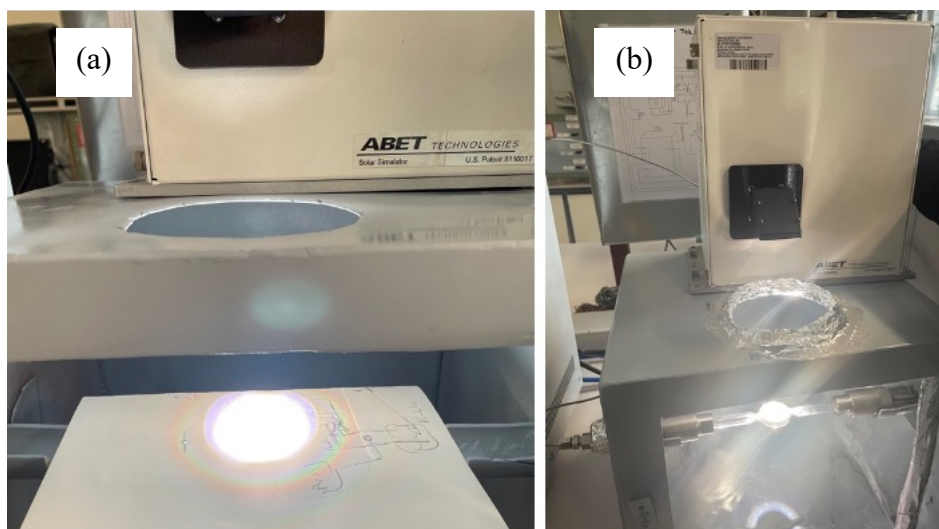


Figure 3.31. (a) 150 W ABET solar simulator, (b) light irradiation on photoreactor.

The 300 W solar simulator device is from Science Tech, and it comes with additional attachments like a focusing lens and an AM1.5 Filter that eliminates UV wavelengths. The difference in light output with and without the focusing lens can be seen from Figure 3.32.

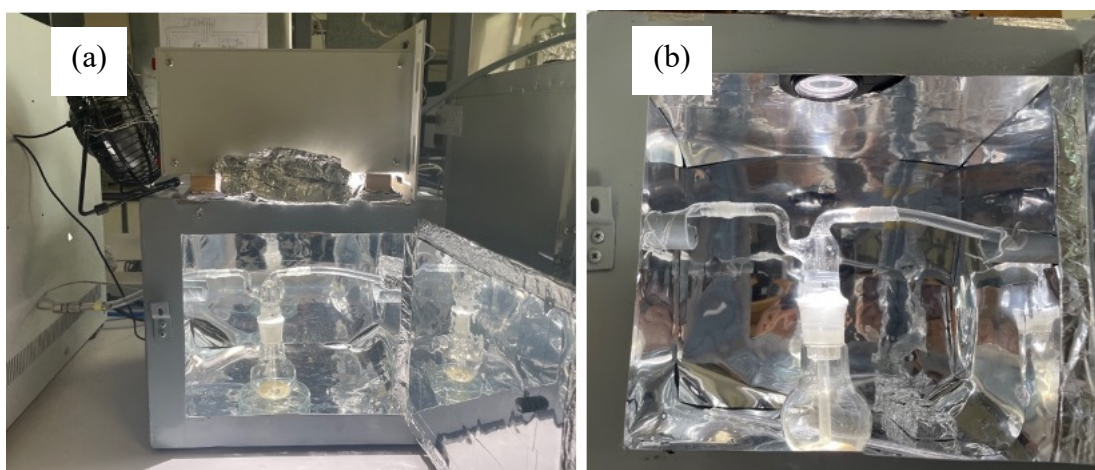


Figure 3.32. 300 W Science Tech solar simulator (a) without, and (b) with the focusing lens.

3.4. Conducted Experiments

This section lists the experiments conducted in the lab after constructing the system. These experiments are referenced by number in the Results and Discussion sections (see chapter 4), where the results obtained from them are analyzed.

The main operating conditions changed in the experiments are the heating of the water in the water bubbler and the volumetric flowrate of feed CO₂ and carrier gas Ar to the system. This is done to better understand the reaction mechanism when certain reactants are not present. The photocatalysts used throughout the experiments are Pt/TiO₂, Pt/TiO₂ + IL, Cu/TiO₂, Cu/TiO₂ + IL, Pt-Cu/TiO₂, and Pt-Cu/TiO₂ + IL. These photocatalysts are tested with the various light sources, feed flowrates, and water vaporization temperature values. The water bubbler and photoreactor designs are also changed throughout the experiments.

Table 3.10. List of conducted experiments and their parameters.

Exp.	Light Type	Photocatalyst	Weight [g]	Water Bubbler	Photoreactor Design	Water Temp. [°C]	Feed Flow [mL/min]
1	UV-Vis1	Pt/TiO ₂	4.4455	WB 1	Tubular (1)	25	CO ₂ : 10 Ar: 40
2	UV	Pt/TiO ₂	4.2842	WB 1	Tubular (1)	25	CO ₂ : 10 Ar: 10
3	UV	Pt/TiO ₂	4.4932	WB 1	Tubular (1)	50	CO ₂ : 10 Ar: 10
4	UV	Pt/TiO ₂	4.8865	WB 1	Tubular (1)	50	CO ₂ : 10 Ar: 10
5	UV	Pt/TiO ₂	4.1937	WB 1	Tubular (1)	50	CO ₂ : 10 Ar: 10
6	UV	Pt/TiO ₂	2.6149	WB 1	Tubular (Thin)	50	CO ₂ : 10 Ar: 10
7	UV	Pt/TiO ₂	2.5309	WB 1	Tubular (Thin)	50	CO ₂ : 5 Ar: 10
8	UV	Pt/TiO ₂	2.4898	WB 1	Tubular (Thin)	60	CO ₂ : 5 Ar: 10
9	UV	Pt/TiO ₂	2.3404	WB 1	Tubular (Thin)	65	CO ₂ : 5 Ar: 10
10	UV	Pt/TiO ₂	1.0000	WB 1	Balloon	50	CO ₂ : 5 Ar: 10
11	UV (out)	Pt/TiO ₂	1.0000	WB 1	Balloon	50	CO ₂ : 5 Ar: 10
12	UV-Vis2	Pt/TiO ₂	1.0036	WB 1	Balloon	50	CO ₂ : 5 Ar: 10

Table 3.10. List of conducted experiments and their parameters (cont.).

13	UV	Cu/TiO ₂	1.0000	WB 1	Balloon	50	CO ₂ : 5 Ar: 10
14	UV	Cu/TiO ₂	1.0000	WB 2	Balloon	50	CO ₂ : 5 Ar: 5
WS 1	UV	Pt/TiO ₂	1.0040	WB 2	Balloon	50	CO ₂ : 0 Ar: 15
15	UV-Vis2	Cu/TiO ₂	1.0000	WB 2	Balloon	50	CO ₂ : 5 Ar: 10
16	UV-Vis2	Pt/TiO ₂	0.9900	WB 2	Balloon	50	CO ₂ : 5 Ar: 10
17	UV	Pt/TiO ₂	1.0024	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
WS 2	UV	Pt/TiO ₂	1.0050	WB 3	Balloon	50	CO ₂ : 0 Ar: 15
18	UV	Pt/TiO ₂	1.0062	WB 3	Balloon	50	CO ₂ : 15 Ar: 0
19	UV-Vis2	Cu/TiO ₂	1.0059	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
20	UV	Cu/TiO ₂	1.0069	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
WS 3	UV	Cu/TiO ₂	1.0044	WB 3	Balloon	50	CO ₂ : 0 Ar: 15
21	UV-Vis2 (F)	Pt/TiO ₂	1.0060	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
22	UV	Cu/TiO ₂	0.9823	WB 3	Balloon	50	CO ₂ : 15 Ar: 0
23	UV-Vis2 (F)	Cu/TiO ₂	1.0030	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
24	UV-Vis2 (F)	Cu/TiO ₂	1.0045	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
25	UV	Cu/TiO ₂ + IL	1.0107	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
26	UV	Cu/TiO ₂ + IL	1.0146	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
27	UV	Pt/TiO ₂ + IL	1.0110	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
28	UV	Pt/TiO ₂ + IL	1.0145	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
29	UV-Vis2 (F)	Pt/TiO ₂	1.0048	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
30	UV-Vis2 (F)	Pt/TiO ₂ + IL	1.0086	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
31	UV-Vis2 (F)	Pt/TiO ₂ + IL	1.0043	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
32	UV-Vis2 (F)	Cu/TiO ₂ + IL	0.9533	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
33	UV-Vis2 (F)	Cu/TiO ₂ + IL	0.9460	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
34	UV	Cu/TiO ₂	1.0071	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
35	UV	Pt/TiO ₂	0.9868	WB 3	Balloon	60	CO ₂ : 5 Ar: 10

Table 3.10. List of conducted experiments and their parameters (cont.).

33	UV-Vis2 (F)	Cu/TiO ₂ + IL	0.9460	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
34	UV	Cu/TiO ₂	1.0071	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
35	UV	Pt/TiO ₂	0.9868	WB 3	Balloon	60	CO ₂ : 5 Ar: 10
36	UV-Vis2 (AM1.5 Filter)	Pt-Cu/TiO ₂	0.0403	WB 3	Balloon	30	CO ₂ : 1 Ar: 0
37	UV-Vis2 (AM1.5 Filter)	Pt-Cu/TiO ₂	0.0406	WB 3	Balloon	50	CO ₂ : 1 Ar: 0
38	UV-Vis2 (AM1.5 Filter)	Pt-Cu/TiO ₂	0.0410	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
39	UV-Vis2 (F)	Pt-Cu/TiO ₂	0.0404	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
40	UV	Pt-Cu/TiO ₂	0.0402	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
41	UV	Pt-Cu/TiO ₂	0.0867	WB 3	Balloon	50	CO ₂ : 5 Ar: 10
42	UV	Pt-Cu/TiO ₂ +IL	0.0401	WB 3	Balloon	50	CO ₂ : 5 Ar: 10

4. RESULTS AND DISCUSSION

To acquire reliable results, the experiments are all conducted in a consistent manner as described here. Before turning on the light source, the photocatalyst is kept in the photoreactor under dark conditions with the reactants flowing over it. Dark conditions are maintained for an hour before light is turned on and the reaction starts. Before dark conditions, both the water bubbler and the photoreactor are purged separately with Ar for around 30 minutes. During dark conditions, Ar and CO₂ flow in the system at a flowrate of 40 ml/min and 5 ml/min, respectively. This applies for all the conducted experiments. After that, the flowrates of Ar and CO₂ are adjusted based on the desired flowrates for each experiment. The first reaction data is taken 1 hour after turning on the light to ensure the establishment of steady state conditions in the system. After that, reaction data is taken from the GC once every 45 minutes (0.75 h).

4.1. Results of Single Metal/TiO₂ Photocatalyst

This section presents the results of Experiments 1–35 utilizing single-metal loaded TiO₂ photocatalysts. The products observed were H₂ and CO with a maximum product yield of 11.79 and 83.72 $\mu\text{mol}/(\text{h.gcat})$, respectively. However, it is important to note that it took longer to notice the presence of CO peaks on the chromatographs generated by the GC. This may potentially be due to having Argon as the carrier gas in the GC column as opposed to using Helium.

After comparing two chromatographs, one taken from a normal experiment and the other from one of the conducted water splitting (WS) experiments (with no CO₂ reactant), it became clear that CO is indeed generated at different points throughout the experiments (Figure 4.1).

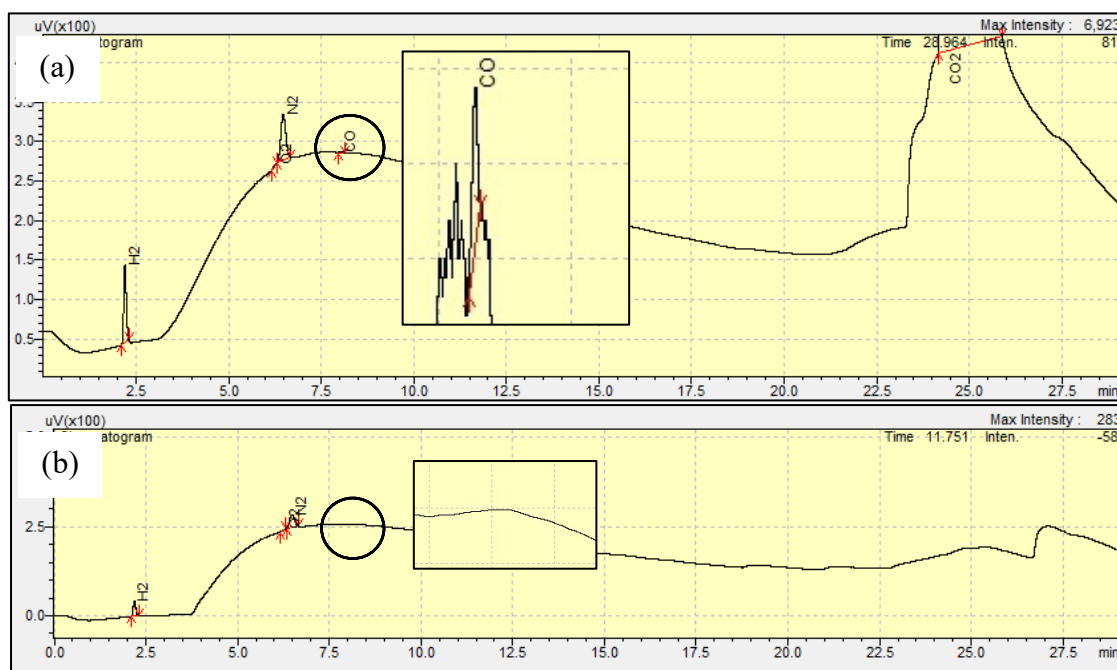


Figure 4.1. CO detection. (a) Chromatograph with CO₂, (b) chromatograph with no CO₂ present (WS exp.).

The other small peaks next to the CO peak are likely to be different uncalibrated gases, or other forms of carbon-based isotopes. However, CO peaks like the one shown in Figure 4.1a were not present all the time. This could be due to the ambiguity of the peaks (apparatus limitations), or it could also be likely that the generation of CO was not very stable with single metal photocatalysts. Thus, the continuous detection of CO was not possible throughout the experiments. Nevertheless, from the gathered data, the CO generation results with recognizable trends are summarized alongside H₂ below.

4.1.1. Pt/TiO₂ Photocatalyst

The plot displayed in Figure 4.2a shows H₂ evolution in units of $\mu\text{mol}/(\text{h.gcat})$ for the first six experiments conducted while Figure 4.2b shows CO evolution starting from Experiment 3, which gave the first detectable and distinguishable CO peaks. A moving average trendline is inserted for each data set (experiment) to get an idea about the CO generation trend taking place. Experiments 1–6 are placed together because they all have the same inlet gas flowrates (CO₂: 10 ml/min, Ar: 10 ml/min) and employ the same photocatalyst (Pt/TiO₂). In Experiment 1, the 150 W solar simulator (UV-Vis1) is used with

no water heating. In Experiment 2, the light is replaced with a UV lamp with no water heating as well. In Experiment 3, a cooling fan is introduced with the UV lamp and water is heated to around 50 °C. In Experiments 4, 5 and 6, the same conditions as Experiment 3 are tested again. All six experiments used the first water bubbler design and all of them, except for Experiment 6, utilized the first photoreactor design (thick tubular reactor). Experiment 6 tested the second photoreactor design (thin tubular reactor).

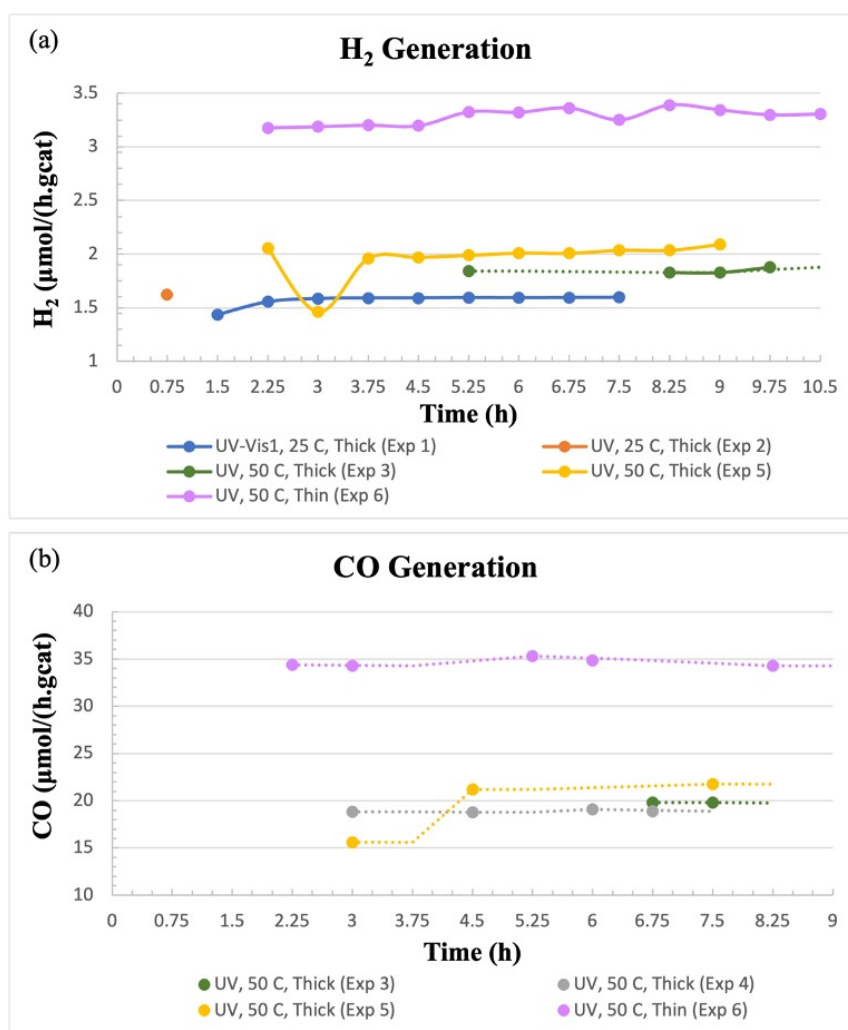


Figure 4.2. (a) H₂ and (b) CO generation for experiments 1–6 (Pt/TiO₂, 10/10 CO₂/Ar).

A few conclusions could be drawn from Figure 4.2a. First, under the applied reactant flowrates, the use of 150 W (UV-Vis1) solar simulator (Experiment 1) generated the least amount of H₂. After one hour of reaction time, no product was observed. H₂ generation began from the second reaction data taken and, although less than the other experiments, continued

in a steady pattern. In Experiment 2 (UV light), only the first data point was slightly larger than the data points of Experiment 1, and then no H_2 was observed. This is most likely due to the excessive amount of heat generated by the UV lamp in the reactor chamber. Thus, a cooling fan is inserted as of Experiment 3. As the system is preliminary and at this point still quite new, an operational error occurred during the time of taking the first 6 data points in Experiment 3, and thus H_2 production could only be observed at the 7th data point (at 5.25 hr), and again at and after the 10th (after 7.5 hr). For this reason, the same conditions were repeated in Experiment 5, which showed better results than Experiment 3, and once more in Experiment 6, which showed the best results.

Heating the water in the water bubbler is an important factor that had a positive effect on the increase in H_2 production after the second experiment. Adjusting the water vaporization temperature basically means adjusting the $\text{H}_2\text{O}/\text{CO}_2$ ratio, which is an important parameter of the process, as it indicates the extent of reactants reaching the photoreactor and interacting with the photocatalyst. As the constructed system was designed for gas-phase photocatalytic CO_2 reduction, heating the water allows a greater amount of “moist” CO_2 gas into the system and thus more room for photoreactions to take place.

The high results attained in Experiment 6, specifically in comparison with the other experiments, are almost certainly attributed to the applied change in photoreactor design. Changing the thick tubular reactor to a much thinner one helped in improving gas–photocatalyst contact while also reducing the amount of excess photocatalyst. The first thick photoreactor design used an average of 4.5 g of photocatalyst, while the second thin design used around 2.5 g per experiment. To increase the gas–photocatalyst contact, both tubular reactor designs were filled completely with the photocatalyst to force the feed gas to flow in between the tight void volume. However, the photocatalyst powder on the sides became more solid and paste-like over time, sticking to the inner edges of the glass bulge and hindering gas to pass through. Thus, reducing the width of the glass bulge in the thinner design helped even out the surface area of the photocatalyst and minimized the negative countereffects. With regards to CO generation (Figure 4.2b), the initial prominent observation is that the scale is much larger, producing a maximum of around 35 $\mu\text{mol}/(\text{h.gcat})$ while the maximum for H_2 is around 3 $\mu\text{mol}/(\text{h.gcat})$. Additionally, from Figure 4.2b, it is clear that the same conclusion stated previously for H_2 regarding

photoreactor design can also be stated for CO generation. Since the thin photoreactor design displayed the highest CO generation as well, it is indeed more efficient than the thick tubular design for the production of both H₂ and CO. Therefore, the proceeding experiments continued with this thin photoreactor. The experiments with the thin photoreactor design using the Pt/TiO₂ photocatalyst are shown in Figure 4.3.

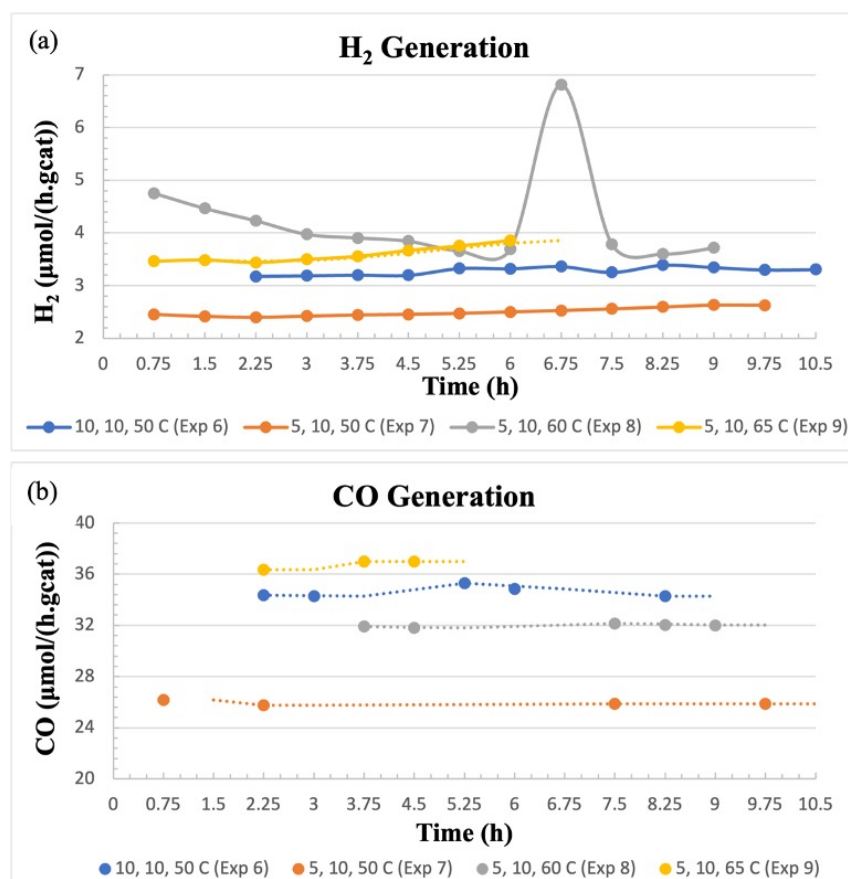


Figure 4.3. (a) H₂ and (b) CO generation using second (thin) photoreactor under different operating conditions (Pt/TiO₂, UV).

All the experiments, except for Experiment 6, operated with reactant flowrates of 5 ml/min and 10 ml/min for CO₂ and Ar, respectively. Experiments 6 and 7 both operated at a water vaporization temperature of 50 °C, while Experiment 8 and Experiment 9 operated at 60 °C and 65 °C, respectively. All thin photoreactor experiments were tested with the UV lamp. The only difference between Experiments 6 and 7 are the reactant flowrates. As there is more CO₂ flowing into the photoreactor in Experiment 6, it can be stated that more product is generated due to the presence of more reactants to begin with. However, by comparing

these results with those of Experiments 8 and 9, it seems that the additional CO₂ is not very significant overall. Variations may also be due to human errors or because of the inconstant heating coming from the hotplate utilized in first water bubbler design.

From Figure 4.3a, Experiment 8 clearly gave the best H₂ results using the thin tubular photoreactor. It operated at 60 °C and 5/10 ml/min flowrates of CO₂/Ar, respectively. Thus, reducing the amount of CO₂ to half that of the Ar carrier gas proved advantageous. Also, the increase in water vaporization temperature to 60 °C allowed for more water vapor to travel to the photoreactor and take part in the photocatalysis process. However, additional heating to 65 °C in Experiment 9 was not too beneficial. Thus, it can be confirmed that water heating is only advantageous up to a certain point. After that, it does not improve the reaction, and might even negatively affect it by adsorbing too much on the photocatalyst surface and leaving little space for CO₂ adsorption. In the case of CO, the initial results present in Figure 4.3b indicate that CO generation increases with increasing water temperature. Also, at the same water temperature of 50 °C, Experiment 6 generated more CO than Experiment 7, indicating that the inlet CO₂ flowrate also affects CO generation. However, unlike the case for H₂ (Figure 4.3a), Experiment 9 (65 °C) generated a higher amount of CO than Experiment 8 (60 °C). Therefore, future research could be performed to find at which water vaporization temperature CO generation decreases, i.e., the optimum water temperature for CO production. Depending on the desirable product (whether H₂ or CO), the operating conditions of the system can be controlled.

Experiment 9 ended after 8 data takings as the amount of air still present in the system at that time was alarming. Therefore, after closing off Experiment 9, the balloon photoreactor (third design) was put in its place in preparation for Experiment 10. Both the thin and the thick tubular reactors suffered from air leakage at the glass and metal parts connecting the photoreactor entrance and exit. The next plot in Figure 4.4 compares the efficiencies of the three photoreactor designs, all using the UV lamp. The best experimental results observed from each design are shown, with Experiment 5 giving the best results using the thick tubular photoreactor, Experiment 8 giving the best results using the thin tubular photoreactor, and Experiment 10 giving the best results using the balloon photoreactor.

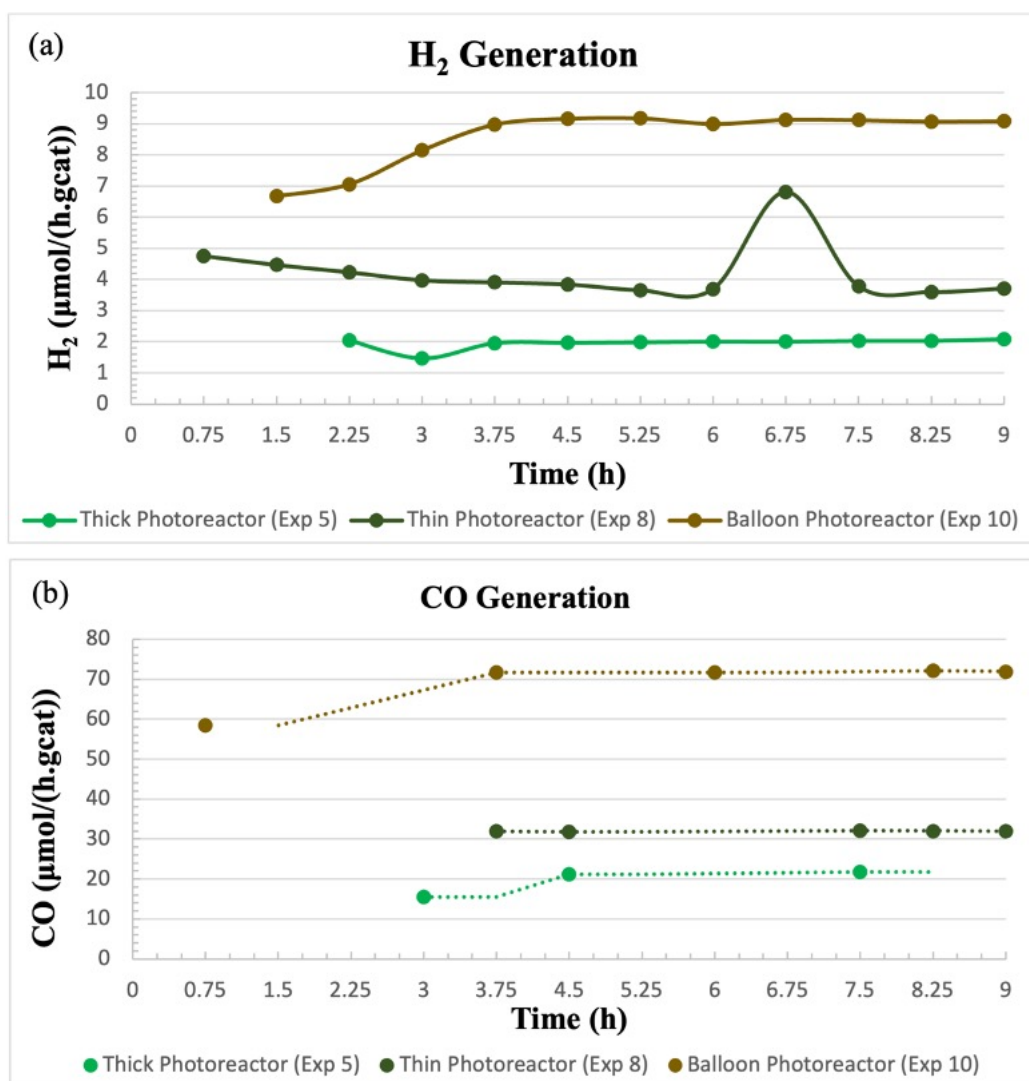


Figure 4.4. Comparing (a) H₂ and (b) CO generation of each photoreactor design (Pt/TiO₂, UV).

The balloon photoreactor (third design) proved to be the most efficient for both products, as even the best results obtained from the other two designs gave significantly lower H₂ and CO production rates. Thus, the subsequent experiments continued with this photoreactor design. The effect of light sources is investigated again with the balloon photoreactor, displayed in Figure 4.5. Experiments 10, 12, and 21 all operated under the same gas inlet flowrates (CO₂: 5 ml/min, Ar: 10 ml/min) and water temperature (50 °C) conditions with the only varying parameter being the light source between them. While Experiment 10 utilized the UV lamp, Experiment 12 used the 300 W solar simulator (UV-Vis2) and Experiment 21 used the 300 W solar simulator with an additional focusing lens

attached (UV-Vis2 (F)). Then, to see how things might change with increased heating and compare the efficiencies of the light sources when the water temperature varies, Experiments 29 and 35 were conducted, also shown in Figure 4.5. Experiments 29 and 35 (yellow and grey) repeated Experiments 21 and 10, respectively, but with a water vaporization temperature of 60 °C instead of 50 °C.

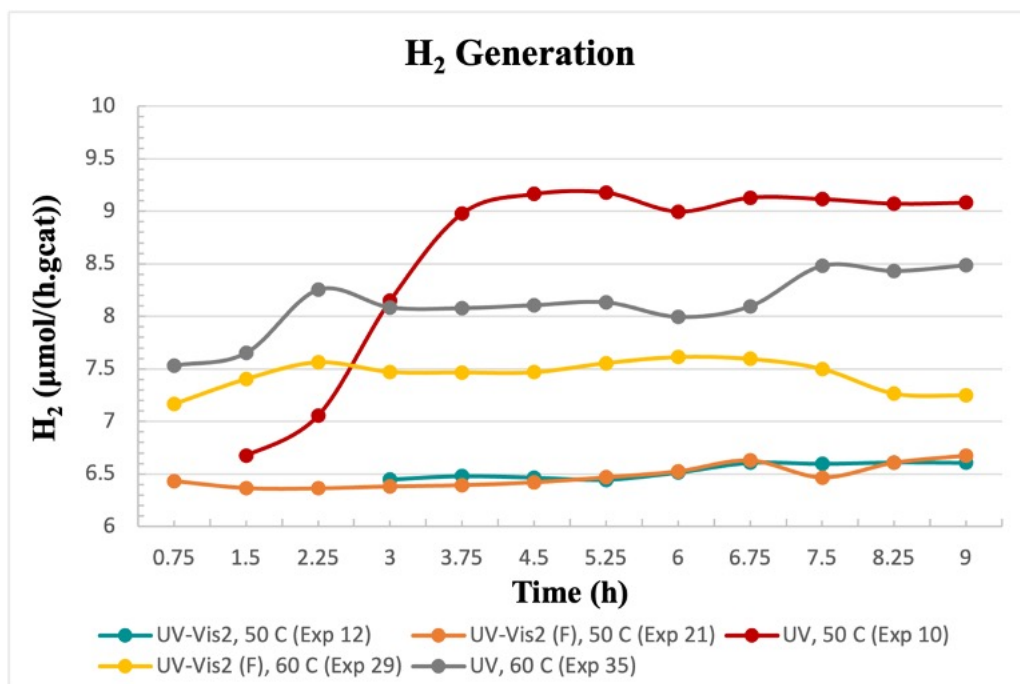


Figure 4.5. H₂ generation under different light sources and water vaporization temperatures (Pt/TiO₂, 5/10 CO₂/Ar).

The results displayed in Figure 4.5 indicate that the Pt/TiO₂ photocatalyst is activated the best under UV light. The differences between Experiments 12 and 21 are very minor, indicating that both light sources lead to similar results in terms of H₂ generation. It is good to note, however, that using the additional focusing lens allowed us to observe H₂ generation from the very first reaction data taken, unlike the case of Experiment 12. Although UV light showed the highest H₂ generation, it can also be confirmed that UV-Vis light works as well.

With regards to varying the water vaporization temperature, different trends are observed for UV-Vis and UV light. With UV-Vis light, the additional heating to 60 °C increased the amount of H₂ produced. However, under UV light, a higher amount of H₂ was

produced at 50 °C instead. Previously, while investigating the thin tubular photoreactor, it was stated that water heating is advantageous up to a certain point, beyond which adverse effects take place. Specifically, it was stated that increasing the water vaporization temperature to 65 °C proved to be disadvantageous, but 60 °C gave better results than 50 °C under UV light. In the case displayed here with the balloon photoreactor, better results were obtained at 50 °C under the same type of light. This could prove to be very advantageous industrially as less water heating would be required to maintain the H₂O/CO₂ ratio that corresponds to 50 °C, once again proving that the balloon photoreactor is more efficient.

The same was investigated for CO, shown in Figure 4.6 on the next page. CO generation also increases with increased temperature of water in this photoreactor design, as both light sources at 60 °C gave a higher amount of CO than both light sources at 50 °C. While the highest H₂ generation was observed at 50 °C using UV light (Figure 4.5), it seems that operating with UV-Vis light at 60 °C is more efficient than UV light at 50 °C in terms of maximizing CO generation. Also, it is worth noting that varying the light source does not have much of an effect on CO generation using the Pt/TiO₂ photocatalyst as much as changing the water vaporization temperature does.

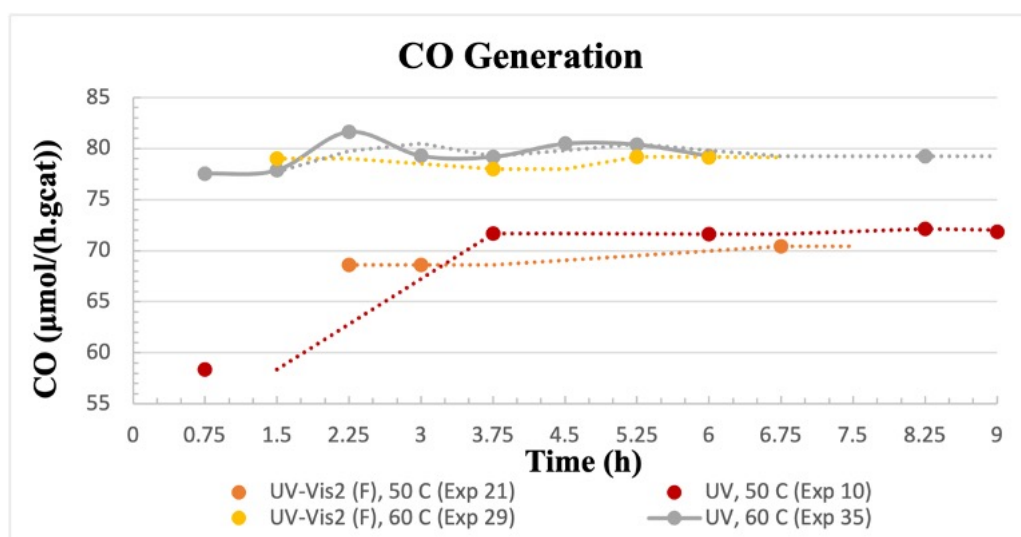


Figure 4.6. CO generation under different light sources and water vaporization temperatures (Pt/TiO₂, 5/10 CO₂/Ar).

The position of the UV lamp was independently investigated in Experiment 11. The UV lamp was held on top of the reactor chamber instead of being placed inside. Aluminum foil was placed on the lamp from the top as to only allow the light to go down to the photoreactor without causing harm to anyone present in the lab. Initially, the aim was to reduce the amount of heat present in the chamber. However, placing the UV lamp in such a way proved to be very disadvantageous, as not only were no products generated, but excessive heat buildup also occurred around the lamp due to the aluminum foil wrapping, causing the outer glass of the lamp to expand. The experiment was stopped shortly after such heating was noticed.

Experiments 14 – 16 utilized the second water bubbler design displayed previously in Figures 3.18 – 3.21, which employs a glass head and a round glass container. No product generation was detected for these experiments. Upon further inspection, testing, and review of the process altogether, it was concluded that the second water bubbler design was not successful in transporting the moist reactant gases to the photoreactor. Water vapor kept condensing on the inner surfaces of the glass head and the glass exit, even with the additional heating cables surrounding them. It was concluded that, to work efficiently, the water bubbler requires the inlet gas pipes to be immersed in the water and the exit pipe must be placed just a few centimeters above the water surface. Stainless steel pipes work the best for this purpose, and thus, the third water bubbler design was implemented. The uniform volume of the cylindrical glass container of the third water bubbler design as well as the addition of the heating cables used instead of the hotplate provided better heating throughout the water bubbler compared to the first design.

As H_2 turned out to be the most stable and consistent product in the experiments so far, the three experiments displayed next in Figure 4.7 were conducted to better understand the reaction mechanism taking place. All three experiments had 50 °C water temperature. Moreover, the UV lamp was used to obtain conspicuous results and see the differences clearly. To serve as a reference, Experiment 17 took place under the normal operating conditions of 5 ml/min and 10 ml/min CO_2 and Ar flowrates (repeating Experiment 10). The day after, Water Splitting Experiment 2 was conducted, where 15 ml/min of Ar was sent into the system with no CO_2 present (0, 15). This experiment was referenced as Water Splitting Experiment 2 previously in section 3.5. since Water Splitting Experiment 1 had been

conducted with the second water bubbler design, which failed to provide results. The aim of this experiment was to test the extent of water splitting occurring in the process. Next, Experiment 18, where only CO₂ is sent into the system at 15 ml/min (15, 0), was conducted to test how the results would change.

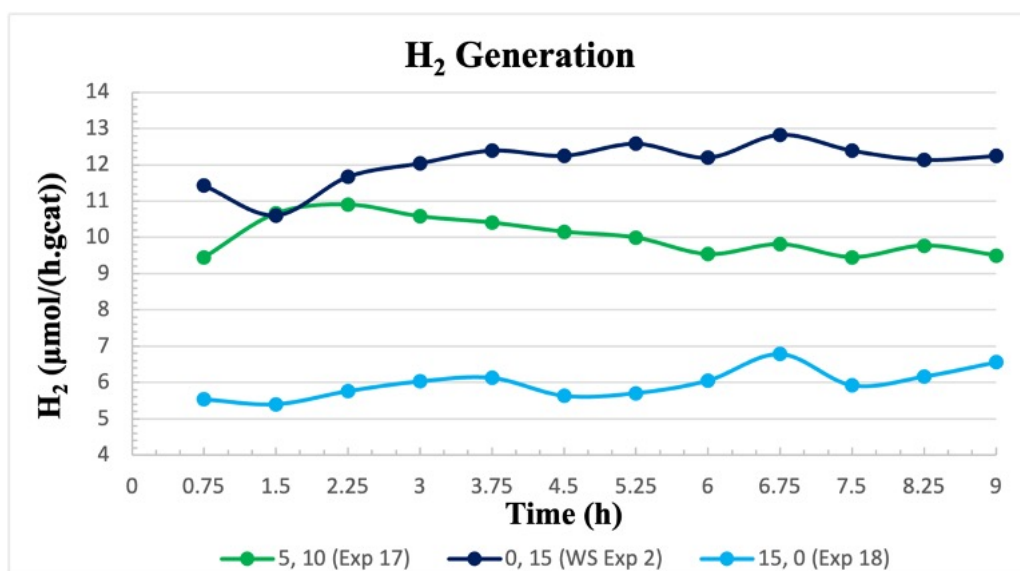


Figure 4.7. Testing the extent of water splitting (Pt/TiO₂, 50 °C water temp., UV).

From the plot (Figure 4.7), several possible conclusions may be drawn. The amount of hydrogen generated in the water splitting experiment being observably higher than the amount generated under the normal conditions of Experiment 17 was expected. However, two different reasons may be behind this. As H₂ is the main precursor for the CO₂ reduction reactions (see Figure 2.6 section 2.2.), it is possible that, under normal operating conditions, a portion of the H₂ generated from water splitting then takes part in other reactions when CO₂ is present. Thus, the amount of H₂ is less in Experiment 17 as part of the H₂ generated from water splitting is used right after. This is also in agreement with the results of Experiment 18, where the H₂ generation is even lower as there is more CO₂ present in the photoreactor to undergo reduction reactions. The other possible reason behind the results in Figure 4.7 may be related to the amount of water vapor present in each experiment. Clearly, it could be stated that a larger amount of H₂ is generated in the water splitting experiment because water vapor is the only reactant in the process. Thus, water vapor adsorbs on the entire surface of the photocatalyst. In Experiments 17 and 18 however, water vapor and CO₂ compete to adsorb on the surface, which affects the quantity of the generated products.

4.1.2. Pt/TiO₂ Photocatalyst Coated with Ionic Liquid

The ionic liquid (IL) coating of photocatalysts has been previously performed and tested in the lab for water splitting experiments. As both water splitting and photocatalytic CO₂ reduction processes can be accomplished using the same photocatalysts, IL coating is also applied here to test its usefulness in the photocatalytic CO₂ reduction process. It has been reported that the use of IL should induce better charge transfer and prevent electron-hole recombination [48]. Four experiments were performed using Pt/TiO₂ + IL photocatalyst, displayed in Figure 4.8. The IL coated photocatalysts were tested under both UV and UV-Vis light sources. Each light source was also investigated twice under both 50 °C and 60 °C water vaporization temperatures.

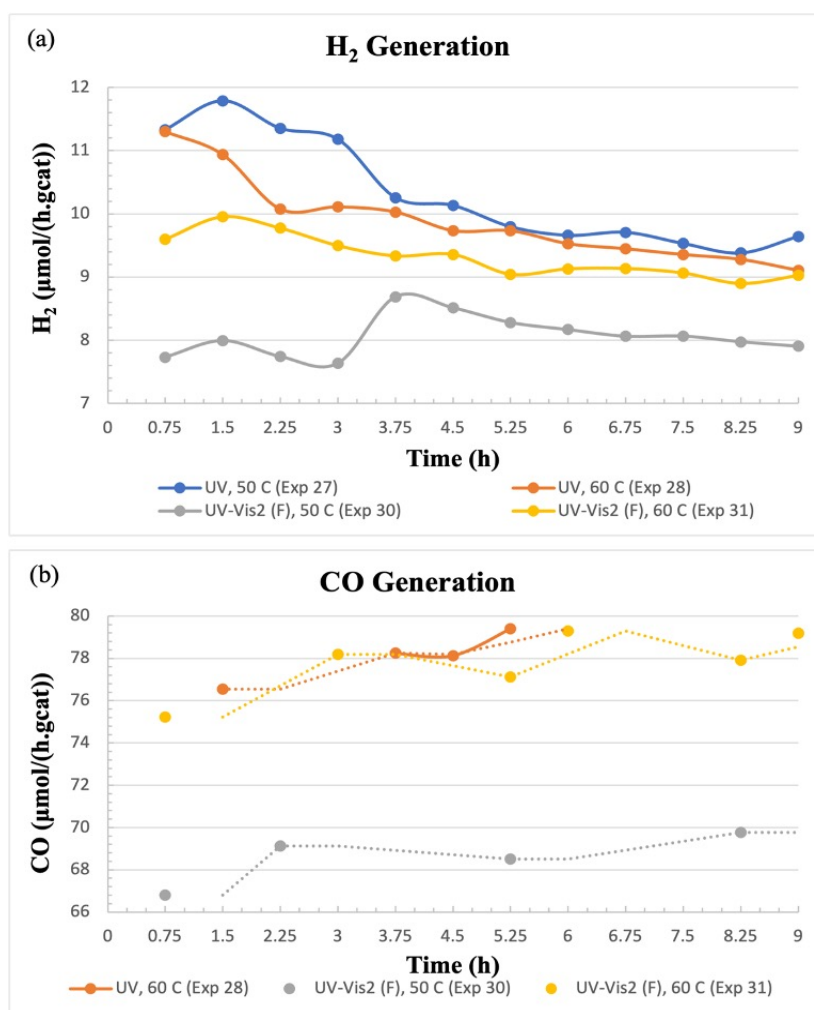


Figure 4.8. (a) H₂ and (b) CO generation under different light sources and water vaporization temperatures (Pt/TiO₂ + IL, 5/10 CO₂/Ar).

In Experiment 27, which operated under UV light at a water vaporization temperature of 50 °C, no distinguishable CO peaks could be detected, thus, it is not present in Figure 4.8b. Nevertheless, as mentioned before, UV light seems to give the highest H₂ generation with the Pt/TiO₂ photocatalyst. However, when coated with the ionic liquid, the hydrogen production seems to decrease in the experiments using UV light, as displayed with the blue and orange lines in Figure 4.8a. This indicates that the IL coated photocatalyst is more prone to decay with time. Additionally, it can also be inferred that increasing water vaporization temperature did not ensure an increase in H₂ generation, just like previously seen without the IL coating using UV light. From the graph (Figure 4.8a), it can be confirmed that with the IL coating, additional water heating to 60 °C is not needed under UV light. In previous experiments using the uncoated Pt/TiO₂ photocatalyst, the same results were observed as well. However, with the IL coating, a higher amount of H₂ could be produced. Previously, without the IL coating (Figure 4.5), the H₂ production range was between 6 – 9.5 μmol/(h.gcat) with the highest product yield being 9.18 μmol/(h.gcat). With the IL coating, the H₂ production range increased to 7.5 – 12 μmol/(h.gcat) and the highest product yield reached 11.79 μmol/(h.gcat). In the case of the focused UV-Vis light utilized in Experiments 30 and 31, the H₂ generation trend remains relatively stable without showing any decline, unlike the UV light experiments shown in the same figure. Moreover, increasing the water temperature from 50 °C to 60 °C also increased the H₂ generation with the UV-Vis light and the results are very close to those obtained using UV with 60 °C water vaporization temperature. These are merely preliminary results that need to be tested further. For example, further testing would need to be performed to find the water temperature after which H₂ generation declines with UV-Vis light.

Again, the trend of increasing CO generation with increasing water vaporization temperature is visible in Figure 4.8b for the coated photocatalyst as well. The highest product yield observed for CO with the IL coating was 79.40 μmol/(h.gcat), which is actually marginally less than the amount obtained without the coating (81.66 μmol/(h.gcat)) from Figure 4.6). This may be due to the GC limitation in detecting CO.

4.1.3. Cu/TiO₂ Photocatalyst

After testing the system with the Pt loaded TiO₂ photocatalyst under different light sources and varying operating conditions, the Cu loaded TiO₂ photocatalyst was tested as well. As the balloon photoreactor proved to be the most efficient and effective, all the experiments mentioned in this subsection were also conducted with this photoreactor. First, like previously done with the Pt/TiO₂ photocatalyst, the effect of different light sources with the Cu/TiO₂ photocatalyst was investigated in terms of H₂ and CO generation in Experiments 13, 19, and 23. Next, Experiments 24 and 34 were conducted to further compare the efficiencies of the light sources when the water vaporization temperature varies (Figure 4.9).

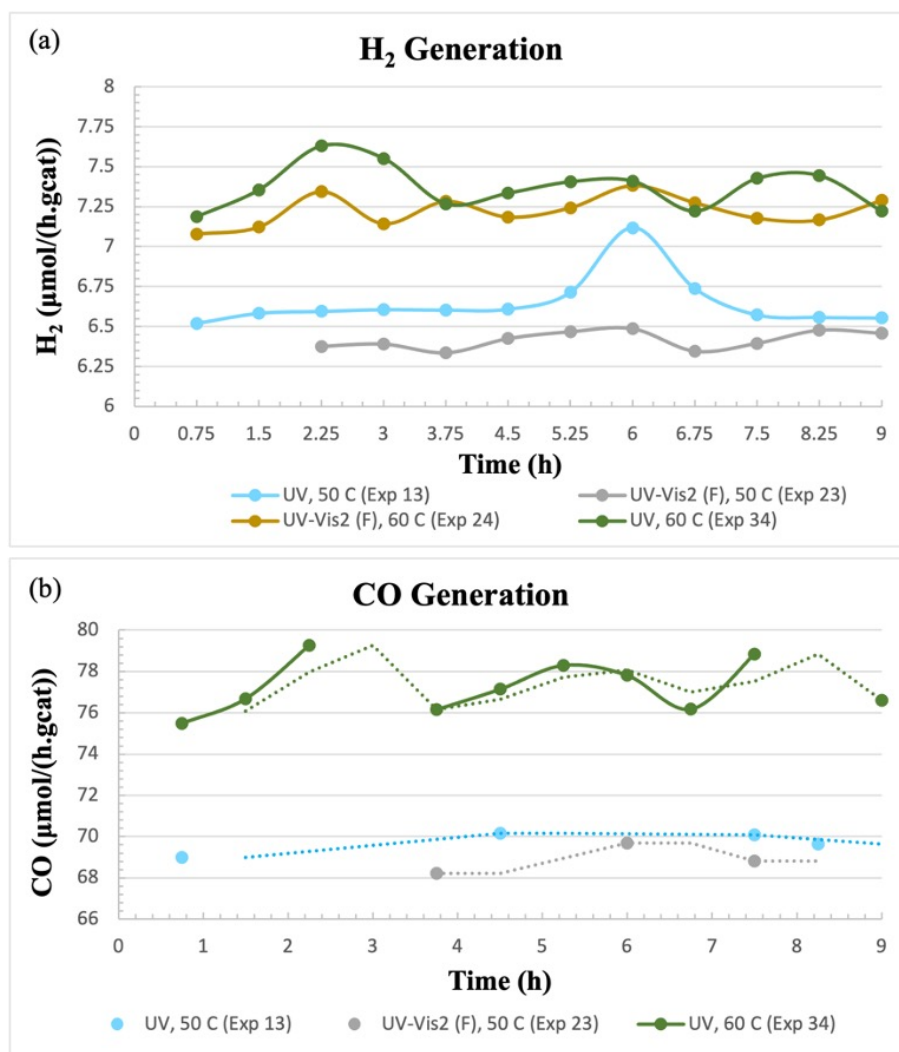


Figure 4.9. (a) H₂ and (b) CO generation under different light sources and water vaporization temperatures (Cu/TiO₂, 5/10 CO₂/Ar).

All of Experiments 13, 19, and 23 were performed under the same gas inlet flowrates (CO_2 : 5 ml/min, Ar: 10 ml/min) and water temperature ($50\text{ }^\circ\text{C}$) conditions with the only varying parameter being the light source. While Experiment 13 utilized the UV lamp, Experiment 19 used the 300 W solar simulator (UV-Vis2) and Experiment 23 used the 300 W solar simulator with the additional focusing lens attachment (UV-Vis2 (F)). The lack of product generation in Experiment 19 is most probably due to some human or environmental errors that occurred that day, as the same conditions were repeated in Experiment 23 with good results. The only change in Experiment 23 was the addition of the focusing lens, which, based on previous experiments, is not the cause behind the huge increase in H_2 generation that was not observed in Experiment 19 (based on observations in previous experiments). Human, environmental, or undetected operational errors could have been the cause behind these results.

If Figure 4.9a were compared with Figure 4.5 (same experiments under Pt/TiO_2), it would become clear that for the Cu/TiO_2 photocatalyst, the different light sources do not have that big of an impact on H_2 generation like they did with the Pt/TiO_2 photocatalyst, where using UV light clearly provided better H_2 generation. From Figure 4.9a, with the exception of the peak shown for UV light at the sixth hour, the results from conducting the same experiment with the same water vaporization temperature under UV light and UV-Vis light are very close.

As also done before with Pt/TiO_2 , the water vaporization temperature was increased from $50\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$ to observe how things might change in Experiments 24 and 34. Likewise, the difference between UV and UV-Vis light is very minimal. However, unlike the Pt/TiO_2 photocatalyst again, better results are observed at increased water heating to $60\text{ }^\circ\text{C}$ using Cu/TiO_2 . Thus, it can be concluded that with the Cu/TiO_2 photocatalyst, the use of UV light and heating to $60\text{ }^\circ\text{C}$ instead of to $50\text{ }^\circ\text{C}$ provides slightly better results.

In terms of CO generation, the results using Cu/TiO_2 as a photocatalyst operating under different light sources and water vaporization temperatures are displayed in Figure 4.9b. Unfortunately, no distinguishable CO peaks could be detected for Experiment 34, which utilized UV-Vis light at $60\text{ }^\circ\text{C}$ water temperature. Experiment 19, which utilized UV-Vis light at $50\text{ }^\circ\text{C}$, also did not show any CO peaks, but as previously mentioned for H_2

generation, that is most likely due to some human or environmental errors, since Experiment 23 repeated the same conditions with good results. The trends displayed in Figure 4.9b are in agreement with both the trends obtained for H₂ using Cu/TiO₂ (Figure 4.9a) and with the previously discussed trends regarding CO generation in general, as 60 °C gave the highest CO generation and the difference between UV and UV-Vis at 50 °C is only around 2 $\mu\text{mol}/(\text{h}\cdot\text{gcat})$.

Again, since H₂ was the main observable product in the experiments so far, another three experiments were conducted to better understand the reaction mechanism taking place when Cu/TiO₂ is used as the photocatalyst (Figure 4.10). Just like the experiments shown before with Pt/TiO₂ in Figure 4.7, these also had 50 °C water temperature and UV lamp as the light source. To serve as a reference, Experiment 20 took place under the normal operating conditions of 5 ml/min and 10 ml/min CO₂ and Ar flowrates (repeating Experiment 13). The day after, Experiment 3 (water splitting) was conducted, where 15 ml/min of Ar was sent into the system with no CO₂ present. Again, the aim was to test the extent of H₂ production when only water splitting was occurring in the process. Next, Experiment 22, where only CO₂ is sent into the system at 15 ml/min, was conducted to see how the results would change.

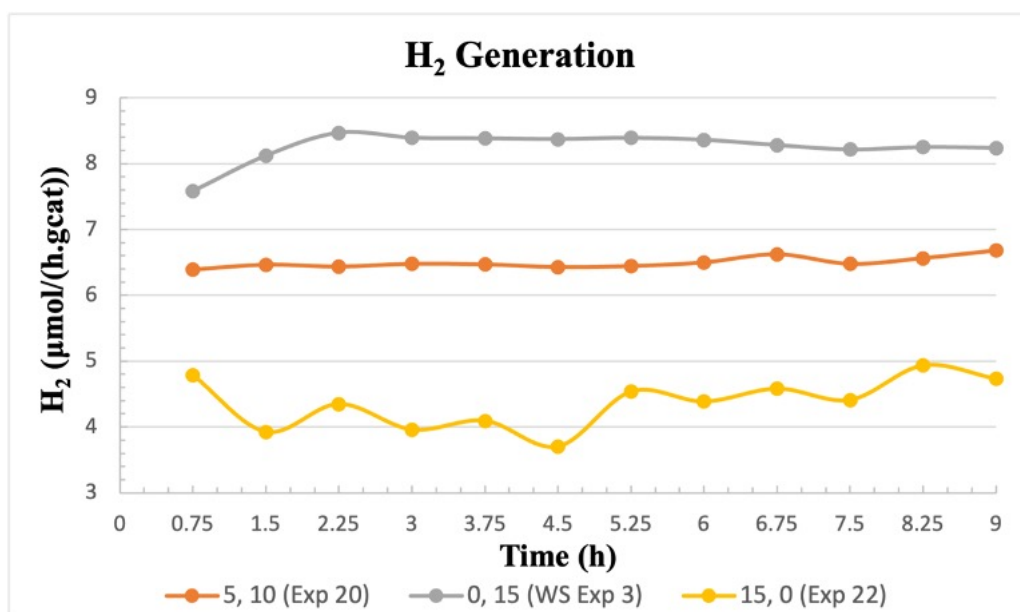


Figure 4.10. Testing the extent of water splitting (Cu/TiO₂, 50 °C water temp., UV).

The results are similar to the ones concluded before with the Pt/TiO₂ photocatalyst. For the same reasons mentioned previously, the amount of H₂ generated in the water splitting experiment is clearly higher than the amount generated under the normal conditions of Experiment 20 and the conditions of Experiment 22. Thus, Figure 4.10 following the same trend as Figure 4.7 shows that the reaction mechanism hypothesized is potentially true for both single metal photocatalysts.

4.1.4. Cu/TiO₂ Photocatalyst Coated with Ionic Liquid

Another four experiments, performed using Cu/TiO₂ + IL photocatalyst, are summarized in Figures 4.11 and 4.12 to test the effect of IL coated Cu/TiO₂ photocatalyst under both UV and UV-Vis2 (F) light sources and under both 50 °C and 60 °C water vaporization temperatures. The inlet flowrates were kept constant throughout the four experiments (5 CO₂, 10 Ar ml/min).

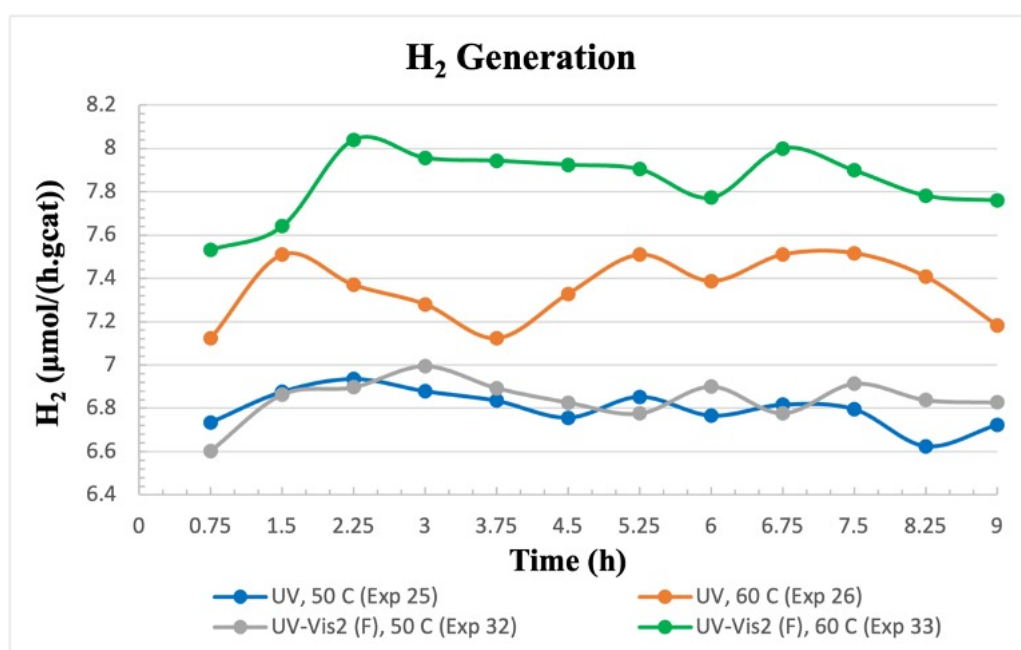


Figure 4.11. H₂ generation under different light sources and water vaporization temperatures (Cu/TiO₂ + IL, 5/10 CO₂/Ar).

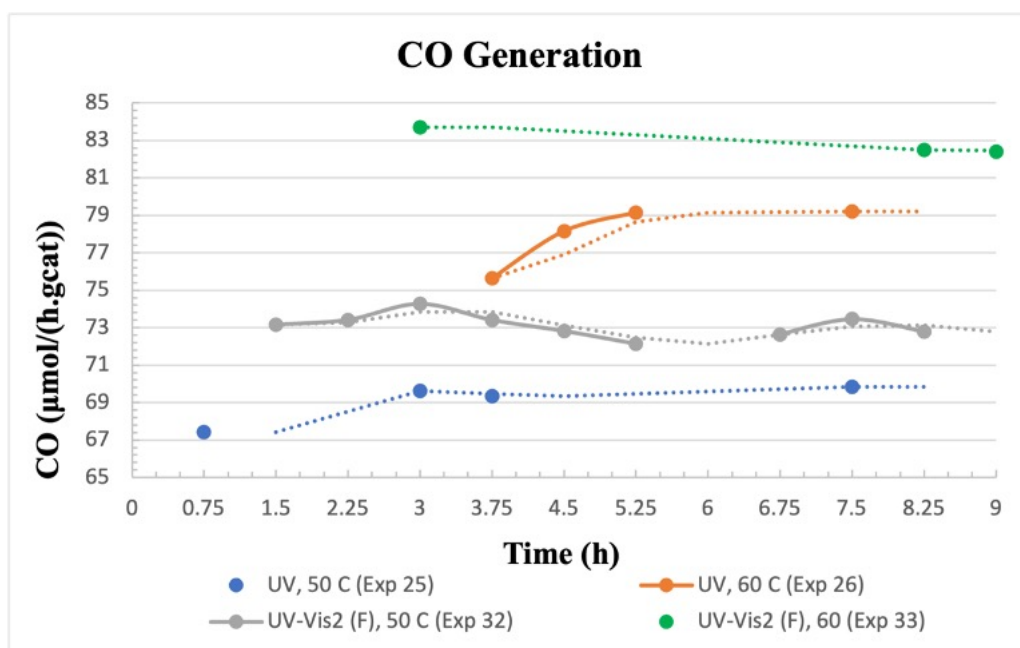


Figure 4.12. CO generation under different light sources and water vaporization temperatures (Cu/TiO₂ + IL, 5/10 CO₂/Ar).

Compared to the Pt/TiO₂ + IL coated photocatalyst (see Figure 4.8a), the trends shown in Figure 4.11 for Cu/TiO₂ + IL are considerably more stable (i.e., no declining trend is observed). The results, in terms of the extent of water heating, agree with the previous results obtained using the uncoated Cu/TiO₂ photocatalyst as well, where it was concluded that the Cu/TiO₂ photocatalyst gives better results at 60 °C rather than at 50 °C. With the ionic liquid coating, however, UV-Vis light proved to be more effective in both H₂ and CO generation than UV light under both heating temperatures. As stated before, the results presented in this thesis are still preliminary, but from them it can be initially concluded that the IL coating on Cu/TiO₂ affects its band gap in a way that helps better include the visible solar spectrum.

4.2. Results of Bimetallic Pt-Cu/TiO₂ Photocatalyst

This section presents the results of Experiments 36 – 42, which utilized a bimetallic Pt and Cu loaded TiO₂ photocatalyst. The main products observed were H₂, CO, and CH₄ with a maximum product yield of 164.76, 1757.29, and 60.26 μmol/(h.gcat), respectively, for each. Like previously stated at the beginning of section 4.1, the continuous detection of CO

was not possible throughout the experiments, although it was detected more after using the bimetallic photocatalyst. Likewise, CH₄ could be detected using the bimetallic photocatalyst but not in a continuous manner throughout the experiments (Figure 4.13).

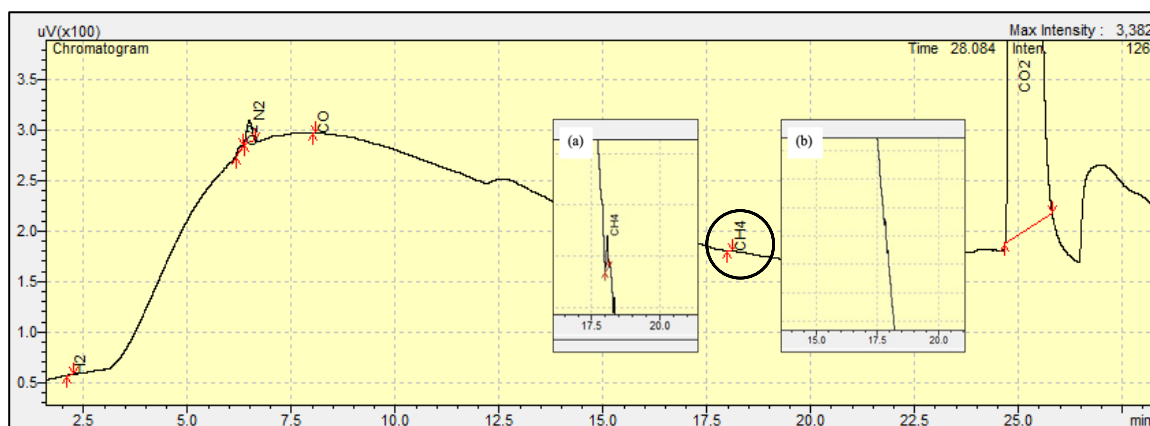


Figure 4.13. GC chromatographs showing (a) CH₄ and (b) traces of CH₄.

The presence of H₂ and CO alongside CH₄ suggests the occurrence of the Fischer-Tropsch reaction for the photocatalytic reduction of CO₂ to methane. The Fischer-Tropsch reaction occurs as opposed to the other possible pathway of successive electron transfer and protonation of CO₂ to form hydrocarbons, which would have been possible if no H₂ or CO was detected with CH₄. The Fischer-Tropsch reaction potentially responsible for the formation of methane in the experiments is shown below [33].



Figure 4.14 on page 79 displays the results of the first three experiments performed with the bimetallic photocatalyst. To test the operability of the system, Experiments 36 and 37 were conducted under the same operating conditions as a reference article [U], which operated under AM1.5 light, 0.04 g photocatalyst weight, and a 1 ml/min flowrate of CO₂ with no Ar carrier gas (1, 0). The reference article did not mention water heating for their water bubbler, so Experiment 36 operated with a 30 °C water vaporization temperature and Experiment 37 operated with 50 °C. After that, Experiment 38 was conducted under the “normal conditions” used in previous experiments (5 ml/min CO₂, 10 ml/min Ar, 50 °C water vaporization temperature) to see how the system operating conditions effect the yield.

Under these conditions, Experiment 38 also used 0.04 g of photocatalyst and established AM1.5 light by adding a filter to the 300 W solar simulator. This way, the only main difference between Experiment 38 and Experiments 36 and 37 was the inlet gas flowrates.

Figure 4.14 (next page) displays the generation results of H₂ (4.15a), CO (4.15b), and CH₄ (4.15c) in $\mu\text{mol}/(\text{h.gcat})$. The results of Experiments 36 and 37 are presented on the left side of the figure on a scale enlarged enough to see the effect of increasing the water vaporization temperature from 30 °C to 50 °C. Experiment 38 is displayed on the right side with the two previous experiments to highlight the huge difference in product yield observed after adjusting the operating conditions (green trendline).

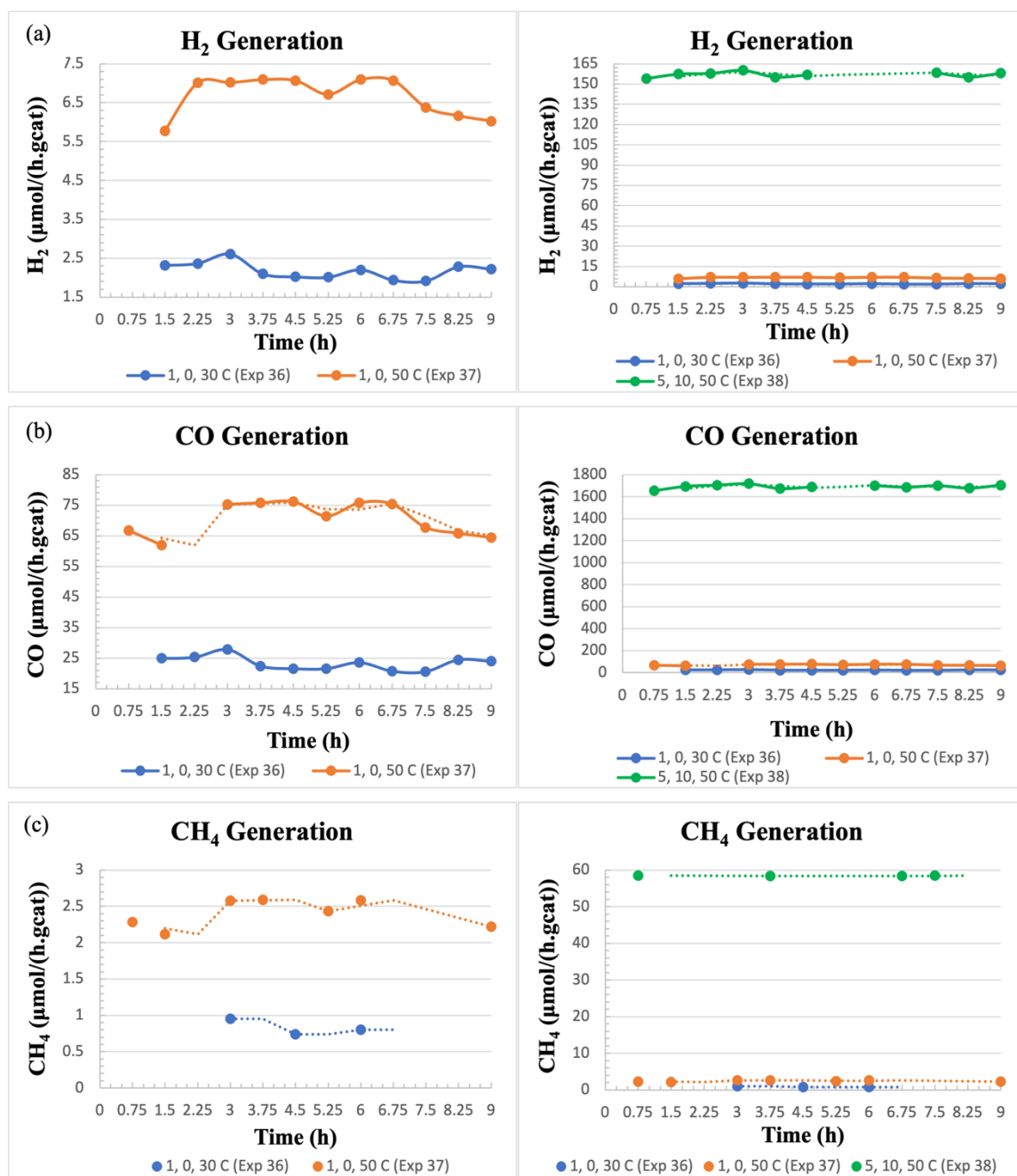


Figure 4.14. Generation of (a) H₂, (b) CO, and (c) CH₄ in experiments 36 – 38 (Pt-Cu/TiO₂, 0.04 g, UV-Vis + AM1.5 Filter).

As shown on the left side of Figure 4.14, the product yields for H₂, CO, and CH₄ almost doubled after increasing the water vaporization temperature from 30 °C to 50 °C. Under the conditions used in the reference article in Experiment 37, the product yield observed for H₂ and CO using the bimetallic photocatalyst was very similar to the product yield observed using the single metal photocatalyst under the normal operating conditions. After adjusting

the operating conditions and implementing the carrier gas again (Experiment 38), the generated amount increased substantially for all three products, as is depicted on the right side of Figure 4.14.

Thus, under the same operating conditions of Experiment 38, Experiments 39 and 40 were conducted using different light sources to examine the effect of light type on the bimetallic photocatalyst. While Experiment 38 tested AM1.5 light, Experiment 39 utilized UV-Vis light (no filter) and Experiment 40 applied UV light. This is displayed in Figures 4.15 and 4.16.

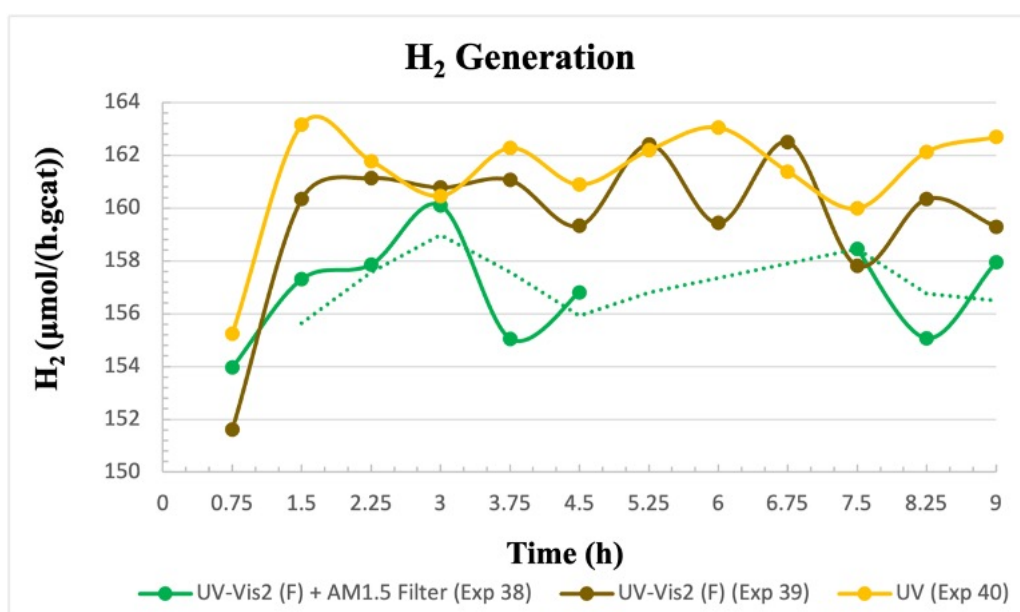


Figure 4.15. Generation of H₂ using different light sources (Pt-Cu/TiO₂, 50 °C water temp., 0.04 g, 5/10 CO₂/Ar).

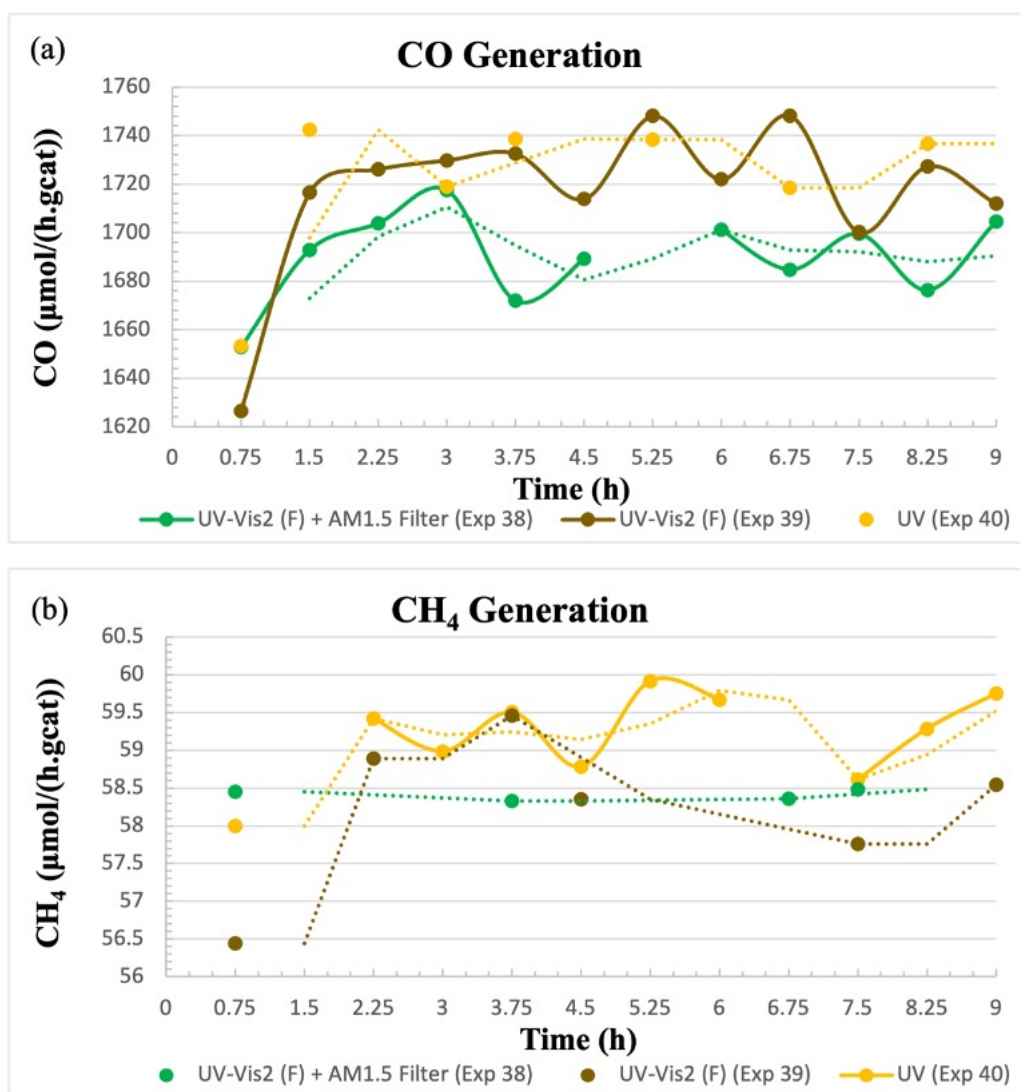


Figure 4.16. Generation of (a) CO and (b) CH₄ using different light sources (Pt-Cu/TiO₂, 50 °C water temp., 0.04 g, 5/10 CO₂/Ar).

Figures 4.15 and 4.16 show similar results for the light types in terms of the generation of the three products with the Pt-Cu/TiO₂ photocatalyst; the difference between the yield obtained from the three light types is not very significant. Therefore, in an industrial and economic perspective, using the AM1.5 light source, which is the closest one to sunlight, could potentially be the most efficient. Even though, since UV light produced the highest H₂ and CH₄ amounts, the next experiments continued with the UV light.

Experiment 41 investigated the effect of increasing photocatalyst weight (around 0.087 g), while Experiment 42 tested the same conditions as before but with an ionic liquid

coating of the bimetallic photocatalyst. The two experiments are displayed alongside Experiment 40 in Figures 4.17 and 4.18, where Experiment 40 serves as a reference experiment having no changes.

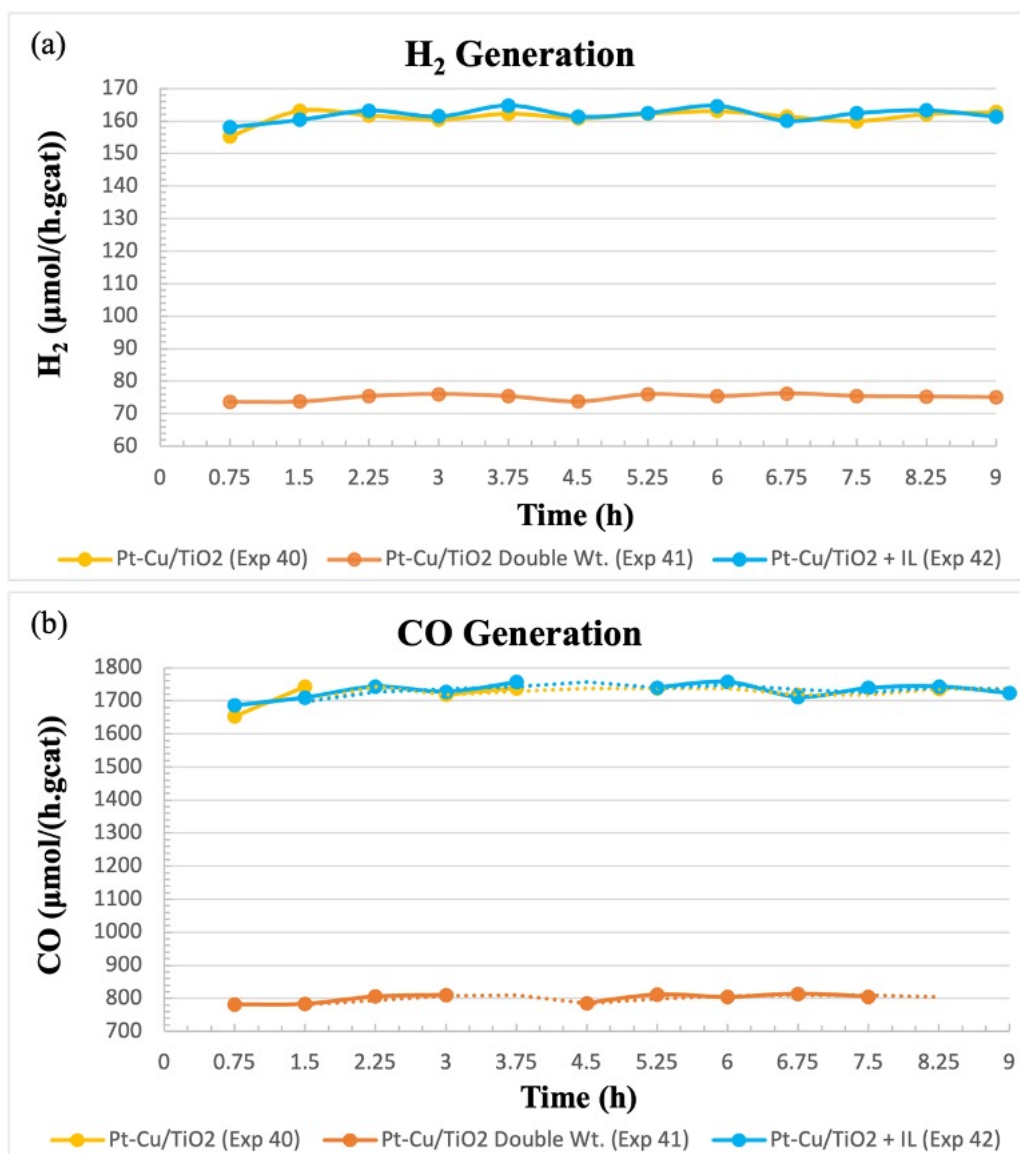


Figure 4.17. Generation of (a) H₂ and (b) CO under increased photocatalyst weight and ionic liquid coating (UV, 50 °C water temp., 5/10 CO₂/Ar).

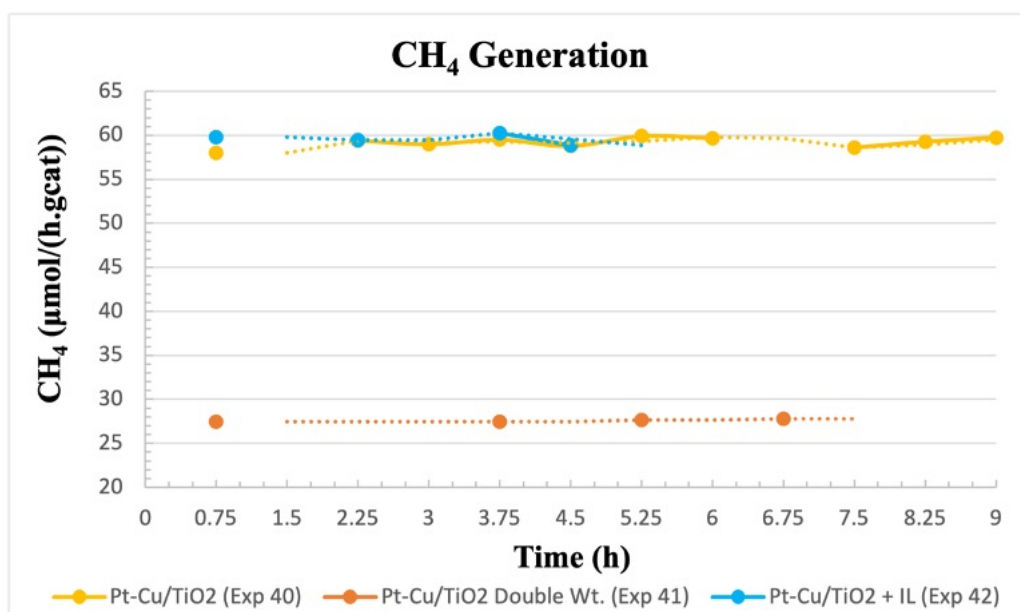


Figure 4.18. Generation of CH₄ under increased photocatalyst weight and ionic liquid coating (UV, 50 °C water temp., 5/10 CO₂/Ar).

From Figures 4.17 and 4.18, it is clear that increasing the photocatalyst weight under the same operating conditions is disadvantageous in terms of yield for all the products. The double photocatalyst weight trendline (orange) is almost half the other two trendlines, indicating that the extra amount of photocatalyst placed in the photoreactor did not take part in the process. This is most probably due to the low reactant–photocatalyst contact area and contact time, as most of the photocatalyst flows to the sides the moment gas starts flowing in the photoreactor (see recommendations in chapter 5).

With regards to IL coating (Experiment 42), the observed increase in product yield for the three products is very marginal, suggesting that, under these conditions, the IL coating does not induce such a significant change in the photoactivity of the bimetallic photocatalyst. As mentioned, the experiments conducted so far in this work are to test the design and operability of the constructed preliminary system, and more experiments are required to be able to understand and enhance the system further.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

In this thesis, a preliminary lab-scale system was designed, constructed, and operated to study the process of photocatalytic CO₂ reduction. Titania-based photocatalysts were prepared and used to test the functionality and viability of the system in generating the desired gas products, which are mainly syngas and methane. Various photoreactor designs, two tubular and one balloon, were tested. Three different water bubbler designs were tested as well. It was found that the balloon glass photoreactor and the third water bubbler design (glass container sealed with a punctured rubber head and surrounded with heating cables, Figure 3.21) proved to be the most effective.

The best results obtained using single metal loaded TiO₂ were 11.79 and 83.72 $\mu\text{mol}/(\text{h.gcat})$ for H₂ and CO, respectively. However, these product yields were not obtained from the same experiment. The highest H₂ product yield of 11.79 $\mu\text{mol}/(\text{h.gcat})$ was obtained over Pt/TiO₂ + IL under UV light with the water vaporization temperature of 50 °C (with no distinguishable CO peaks detected). On the other hand, the highest CO product yield of 83.72 $\mu\text{mol}/(\text{h.gcat})$ was obtained over Cu/TiO₂ + IL photocatalyst under focused UV-Vis light and the water vaporization temperature of 60 °C (with H₂ production of 7.96 $\mu\text{mol}/(\text{h.gcat})$). Inlet gas flowrates for both were 5 ml/min CO₂ and 10 ml/min Ar.

The best results obtained using bimetallic loaded TiO₂ were 164.76, 1757.29, and 60.26 $\mu\text{mol}/(\text{h.gcat})$ for H₂, CO, and CH₄, respectively. These product yields were all obtained from the same experiment, which operated over Pt-Cu/TiO₂ + IL photocatalyst under UV light and the water vaporization temperature of 50 °C. The inlet gas flowrates were 5 ml/min CO₂ and 10 ml/min Ar as well.

5.2. Challenges and Recommendations

Several challenges were encountered throughout this work while several areas require some improvement. One of the main challenges was the GC column used (Restek, Packed Column C40136-02). As stated in the previous chapter, the CO and CH₄ peaks obtained from the GC chromatographs were often quite undistinguishable and hard to be detected. Moreover, other unspecified peaks were obtained at random points and times on the chromatographs, indicating that there might be a potential problem with the column. Therefore, it is recommended to continue any future experiments after performing a thorough cleaning of the column or use a new/different one to minimize this limitation. Another challenge faced during the experiments was the constant presence of air (mainly N₂) in the system. Even though both the water bubbler and the photoreactor were separately purged with Ar for around 30 minutes before initiating dark conditions, a certain amount of air remained in the system during the experiments. Although leak tests were performed at the beginning of every experiment, this indicates that a hidden potential leak is still present in the system. It should be noted, however, that after the balloon photoreactor was used instead of the tubular ones, the amount of air considerably decreased but it never became zero. It is thus recommended to investigate this further to avoid any leakage of the desirable product gases.

Three photoreactor designs were presented in chapter 3 and tested in chapter 4. However, the photoreactor design still requires enhancement in terms of increasing gas-photocatalyst contact area. As shown in Figure 5.1, the differences in color of the photocatalyst taken after the termination of the experiment indicates that not all of it undergoes the process equally.



Figure 5.1. Differences in photocatalyst color after reaction termination.

Figure 5.1 shows the balloon photoreactor loaded with 1 g of photocatalyst. The differences in color may also indicate that with this photoreactor design, a loading of 1 g of photocatalyst may be too much. However, the problem with a further decrease in the photocatalyst weight is losing the photocatalyst upon initiating flow, which causes the photocatalyst to move to the sides. This occurred when 0.04 g of the bimetallic photocatalyst was loaded, as shown in Figure 5.2, where the surface directly underneath the gas inlet became completely empty upon starting gas flow. In other words, the photocatalyst was dragged by the inlet gases.

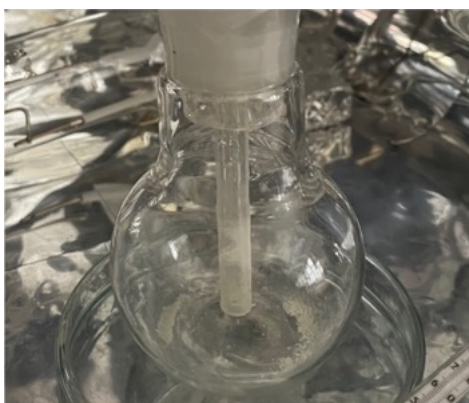


Figure 5.2. Uneven photocatalyst distribution after starting gas flow.

Thus, better contact for the gas-phase process is necessary to ensure an even and effective photocatalyst distribution in the photoreactor and maximize the overall efficiency

of the process. This may be solved by utilizing nano-porous glass discs that are fritted as to only allow gases to pass through. Placing the photocatalyst on such discs in the photoreactor and allowing the gas to pass through the disc and exit from underneath it could substantially improve the gas-photocatalyst contact area and contact time. Figure 5.3 shows examples of such glass fritted discs.

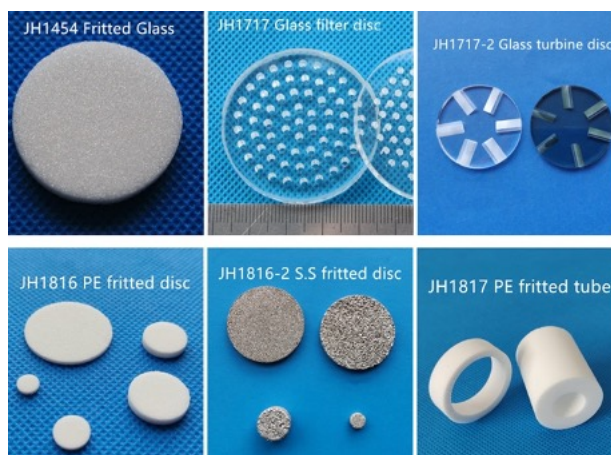


Figure 5.3. Various fritted glass discs. [49]

In terms of photocatalyst enhancement, several recommendations could be presented since this work focused more on the construction and testing of the system rather than on the photocatalyst itself. The main recommendations are listed below.

- Varying the loading of Pt and Cu on TiO_2 and testing its effect on product selectivity (as Pt/ TiO_2 proved to prompt the generation of more H_2 while Cu/ TiO_2 proved to be more selective towards producing CO).
- Loading of other metals or other metal combinations. For example, Au becomes very reactive when in nano-size.
- Different synthesis methods could be tested instead of the ones mentioned in section 3.2. (Incipient-to-wetness impregnation, DPU, Photo-deposition) as the photocatalyst is largely affected by its preparation method.
- Adjusting the crystal lattice of TiO_2 via doping rather than simple metal loading (impregnation), surface sensitizing using dyes, or creating other composites using TiO_2 -based materials could be investigated.

- Coating TiO_2 on monolith support to increase surface contact area and photoactivity.

In terms of process enhancement, the following recommendations could be the focus of future works:

- Testing of other operating conditions (i.e., different reactant flowrates and water vaporization temperatures).
- Testing the effect of a shift from continuous to batch or semi-continuous (pulse-wise) operation.
- Develop new photoreactor designs that ensure better gas-photocatalyst contact and geometrically better accommodate the incoming light irradiations.
- Install a heat exchanging system with or around the photoreactor to maintain the desired reaction temperature (heat removal system).
- Testing the effect of inputting H_2 with the feed on the hydrocarbon (CH_4) yield.

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