PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE AND METHANE USING PLASMONIC PROPERTY OF SILVER/TITANIA NANOPARTICLES

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A thesis submitted in fulfilment of the
requirements for the award of degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

JULY 2017

This thesis is dedicated to

my beloved parents

for their endless love, patience, support, constant encouragement over the years, and for their prayers

ACKNOWLEDGEMENT

"All praises and glory to ALMIGHTY ALLAH, who is most gracious and very merciful and his countless blessings on us who always helped me to complete my project"

Writing this Ph.D. dissertation has only been possible with the precious support, help and encouragement of several individuals. I am sincerely grateful to my professors, lecturers, staff, family and friends, and most of all, my supervisor, who have all accompanied me on this journey.

I wish to first acknowledge my supervisor Prof. Ir. Dr. Nor Aishah Saidina Amin, for the guidance and suggestions offered during my research and study at Universiti Teknologi Malaysia (UTM). A main source of motivation throughout my study and research has been her constant energy and enthusiasm. I have learned from my supervisor to see and confront challenges in uncountable ways and from various perspectives. She has always stimulated me to do my best and not be disappointed, by giving me tremendous hope in any consultation regarding my project.

I am very grateful as well to my co-supervisor from Pasteur Institute of Iran, Assoc. Prof. Dr. Seyed Nezamedin Hosseini. I have benefited greatly from his guidance and valuable suggestions by email or in person when I was in Iran.

Heartfelt thanks to Universiti Teknologi Malaysia (UTM), and particularly the Faculty of Chemical and Energy Engineering (FCEE) as well as the postgraduate staff for the positive feedback, cooperation and valuable discussions. I also thank the Chemical Reaction Engineering Group (CREG) members and UTM friends for their support and input pertaining to this research.

Last but not least, and very importantly, I am extremely grateful to my parents, brothers and sisters for their huge help, support, appreciation, love, encouragement and many prayers along my study and throughout my life. I am very thankful to my very sweet family. I could not have done it without you all. Thank you Mom and Dad for everything! Love you.

ABSTRACT

Human industrial undertakings have rendered carbon dioxide (CO_2) and methane (CH_4) as key greenhouse gas constituents. Greenhouse gases aggravate global warming considerably along with the greenhouse effect. Catalyzed reaction of CO_2 with CH_4 to produce valuable chemicals has received increasing attention from both environmental and industrial players. Photocatalysis seems to be an encouraging method of realizing green chemistry objectives through reducing the concentrations of predominant greenhouse gases, especially CO_2 and CH_4. One of the biggest challenges in the study of photocatalysts is to achieve new catalysts with high activity in the visible light range. Noble metal nanoparticles are known to absorb visible light extremely well due to the surface plasmon resonance (SPR) effect characterized by the strong field enhancement at the interface. Therefore, it is possible to attain chemical reactions with a significant fraction of the entire solar spectrum. In this study, immobilized silver/titania (Ag/TiO_2) nanoparticles were coated on stainless steel webnet by dip-coating method to enhance the visible light plasmonic photocatalyst and reduce CO_2 in the presence of CH_4 under ultraviolet-visible (UV-Vis) light irradiation. The synthesized catalysts were characterized using x-ray diffraction, field emission scanning electron microscopy, energy dispersive x-ray, transmission electron microscopy, Fourier transform infrared, nitrogen adsorption-desorption isotherm, UV-Vis spectrophotometry, Raman spectrometry, temperature programmed desorption of carbon dioxide and photoluminescence analysis techniques. P25 titania nanoparticle model served as the photocatalyst due to the large surface area with CO_2, CH_4 and nitrogen as feeds in the batch photoreactor. Experimental results revealed that the photocatalytic activity for the conversion of CH_4 and CO_2 under UV-Vis light irradiation over Ag-loaded TiO_2 was better than that of pure TiO_2 due to the synergistic effect between light excitation and SPR enhancement. Response surface methodology was applied for analysis and optimization to achieve the highest conversion of CO_2 and CH_4. The optimal process parameter values were 9 h for irradiation time, 4 wt% for Ag-loaded, an equal initial ratio of CO_2:CH_4 and 100 mesh size. The maximum conversion of CO_2 and CH_4 in optimal condition was achieved at 29.05% and 34.85%, respectively. In addition, the photon energy in the UV-Vis range was high enough to excite the electron transition in Ag/TiO_2 to produce some hydrocarbons and oxygenates, such as ethane (C_2H_6), ethylene (C_2H_4), acetic acid and formic acid. During the reaction, the maximum yields of C_2H_6 and C_2H_4 achieved were 1500.52 and 1050.50 $\mu mole.gcat^{-1}$, respectively. Furthermore, the Ag/TiO_2 plasmon photocatalyst exhibited great reusability with almost no change after three runs. Finally, a kinetic model was developed based on the Langmuir–Hinshelwood mechanism to model the hydrocarbon formation rates through the photocatalytic reduction of CO_2 with CH_4. The experimental data fit well with the kinetic model. Based on the findings, these nanostructured materials are considered promising and effective photocatalysts for conversion of CO_2 and CH_4 into high-value products.

ABSTRAK

Kerja-kerja perindustrian manusia menyebabkan pengeluaran karbon dioksida (CO_2) dan metana (CH_4), juzuk utama gas rumah hijau. Gas rumah hijau memburukkan lagi pemanasan global bersama dengan kesan rumah hijau. Tindak balas bermangkin CO_2 dengan CH_4 untuk menghasilkan bahan kimia berharga semakin mendapat perhatian daripada kedua-dua perspektif alam sekitar dan industri. Fotopemangkinan tampak seperti satu kaedah yang menggalakkan perealisasian objektif kimia hijau melalui pengurangan kepekatan gas-gas rumah hijau utama, terutamanya CO_2 dan CH_4. Salah satu cabaran terbesar bagi kajian fotopemangkinan adalah untuk menyediakan pemangkin baharu dengan aktiviti yang tinggi dalam penyinaran cahaya nampak. Nanozarah logam adi diketahui menyerap cahaya nampak dengan sangat baik kerana kesan permukaan plasmon resonans (SPR) dicirikan oleh peningkatan medan kuat pada antara muka. Oleh itu, untuk menjalankan tindak balas kimia dengan sebahagian besar keseluruhan spektrum matahari adalah tidak mustahil. Dalam kajian ini, nanozarah argentum/titania (Ag/TiO_2) tersekat gerak disalut pada webnet keluli tahan karat disediakan dengan kaedah celup-salutan untuk meningkatkan fotopemangkin plasmonik cahaya nampak bagi mengurangkan CO_2 dengan kehadiran CH_4 di bawah penyinaran cahaya nampak-ultraungu (UV-Vis). Bahan-bahan disintesis dicirikan dengan menggunakan analisis teknik-teknik pembelauan sinar-x, mikroskop elektron pengimbas pancaran medan, tenaga serakan sinar-x, mikroskop penghantaran elektron, inframerah transformasi Fourier, isoterma penjerapan-nyahjerapan nitrogen, spektrofotometer UV-Vis, spektrometer Raman, suhu nyahjerapan diprogramkan karbon dioksida, dan fotopendarkilau. Nanozarah titania model P25 digunakan sebagai fotopemangkin kerana luas permukaan yang besar dengan CO_2, CH_4 dan nitrogen sebagai suapan dalam reaktor foto kelompok. Hasil kajian menunjukkan aktiviti fotopemangkin bagi penukaran CH_4 dan CO_2 di bawah penyinaran cahaya UV-Vis menunjukkan TiO_2 Ag-dimuatkan adalah lebih baik daripada TiO_2 tulen kerana kesan sinergi antara pengujaan cahaya dan peningkatan SPR. Kaedah permukaan tindak balas digunakan untuk menganalisis dan pengoptimuman bagi mencapai penukaran CO_2 dan CH_4 tertinggi. Nilai-nilai optimum parameter proses adalah 9 jam masa penyinaran, 4 wt% bagi Ag-dimuatkan, nisbah permulaan yang sama bagi CO_2:CH_4, dan saiz mesh 100. Penukaran maksimum CO_2 dan CH_4 pada keadaan optimum masing-masing dicapai pada 29.05% dan 34.85%. Di samping itu, tenaga foton dalam julat UV-Vis cukup untuk merangsang peralihan elektron dalam Ag/TiO_2 bagi menghasilkan beberapa hidrokarbon dan oksigenat yang dihasilkan seperti etana (C_2H_6), etilena (C_2H_4), asid asetik, dan asid formik. Pada masa tindak balas, hasil maksimum C_2H_6 dan C_2H_4 masing-masing dicapai pada 1500.52 dan 1050.50 $\mu mol.gcat^{-1}$. Selain itu, fotopemangkin plasmon Ag/TiO_2 menunjukkan kebolehgunaan semula dengan hampir tiada perubahan selepas tiga larian. Akhir sekali, model kinetik dibina berdasarkan mekanisme Langmuir-Hinshelwood untuk memodelkan kadar pembentukan hidrokarbon melalui pengurangan fotopemangkin CO_2 dengan CH_4. Data uji kaji dalam kajian ini mempunyai padanan yang baik dengan model kinetik. Berdasarkan dapatan kajian, bahan-bahan berstruktur nano dapat dianggap sebagai fotomangkin berpotensi dan berkesan untuk penukaran CO_2 dan CH_4 kepada produk bernilai tinggi.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
BBD	-	Box-Behnken Designs
BET	-	Brunauer-Emmett-Teller
BJH	-	Barrett-Joyner-Halenda
CB	-	Conduction Band
CH_4	-	Methane
CO_2	-	Carbon dioxide
DF	-	Degree of freedom
DOE	-	Design of Experiments
EDX	-	Energy Dispersive X-ray
FE-SEM	-	Field Emission Scanning Electron Microscope
FID	-	Flame Ionization Detector
FWHM	-	Full Width at Half Maximum
GC	-	Gas Chromatograph
GHG	-	Greenhouse Gases
HPLC	-	High performance liquid chromatography
HRTEM	-	High-resolution transmission electron microscopy
IPCC	-	Intergovernmental Panel on Climate Change
L-H	-	Langmuir-Hinshelwood
LSPR	-	Local Surface Plasmonic Resonance
MFC	-	Mass Flow Controller
MS	-	Mean squares
NPs	-	Nanoparticles
PL	-	Photoluminescence
ppm	-	Parts per million
RSM	-	Response Surface Methodology
SS	-	Sum of squares

TCD	-	Thermal Conductivity Detector
TEM	-	Transmission Electron Microscopy
TiO_2	-	Titania
TNPs	-	Titania Nanoparticles
TPD	-	Temperature Programmed Desorption
UV	-	Ultraviolet
VB	-	Valence Band
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

Å	-	Angstrom
C	-	Speed of light
℃	-	Degree Celsius
d	-	Lattice fringe
E_g	-	Bang gap energy
e^-/h^+	-	electron/hole
h	-	Hour
h	-	Planck constant
hv	-	Photon energy
I	-	Intensity
J	-	Joules
keV	-	Kiloelectron-Volt
k_i	-	Kinetic constant
min	-	Minutes
N_A	-	Avogadro's number
nm	-	Nanometer
p_i	-	Partial pressure
R^2	-	Regression coefficient
W	-	Watt
wt%	-	Weight percentage
Y_{CH4}	-	Conversion of CH_4
Y_{CO2}	-	Conversion of CO_2

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Environmental pollution comes from many different sources and most governments are taking environmental protection very seriously. The situation is such that people in a particular city or even country may even be affected by pollution from neighboring countries. Carbon dioxide (CO_2) emission has become a major challenge worldwide due to the rising CO_2 levels in the atmosphere. Greenhouse gases (GHG) trap heat in the atmosphere, causing global warming. Recent human-induced impact on forestry and other land use has led to the addition of several types of greenhouse gases in the atmosphere. The main GHGs in the Earth's atmosphere are carbon dioxide (CO_2), methane (CH_4), nitrous oxide, water vapor and ozone. CO_2 is considered the largest contributor to GHG. Figure 1.1 presents details about the major greenhouse gases. In this chart, the size of a part represents the amount of warming contributed by each type of gas to the atmosphere as a result of current emissions from human activities (IPCC, 2014). According to the IPCC, average greenhouse gas concentrations have reached the highest global levels documented and are not ceasing to rise. Figure 1.2 demonstrates atmospheric concentrations of CO_2 (green), CH_4 (orange) and N_2O (red) from direct atmospheric measurements of GHG until 2010. The concentration of CO_2 as a major component of GHG reached 389 ppm in 2010 and 391 ppm in 2011, but these values are not included in the chart (Allen *et al.*, 2014).

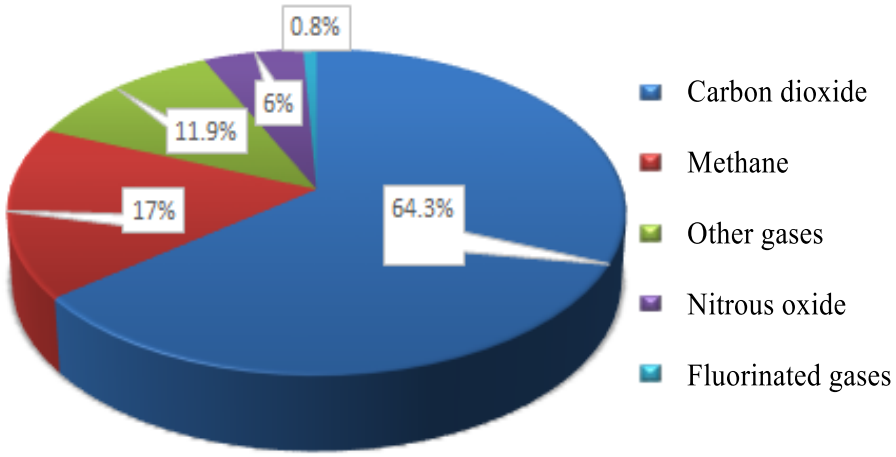

Figure 1.1 Major Greenhouse gases (IPCC, 2014)

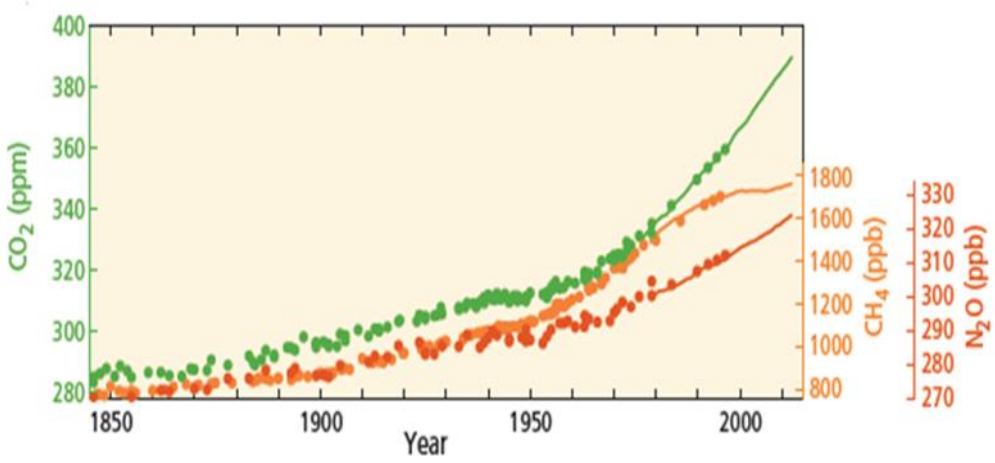

Figure 1.2 Globally averaged greenhouse gas concentrations (Allen *et al.*, 2014)

IPCC reported that fossil fuel use has led to increasing environmental pollution, with greenhouse gas concentrations rising over time (Qin *et al.*, 2011). Human activities release carbon dioxide mainly through greenhouse gas emissions, but the human impact on other gases such as methane is not negligible. Figure 1.3 shows the global anthropogenic CO_2 emissions from forestry and other land use, fossil fuel burning, cement production and flaring. On the other hand, IPPC has stated that the global GHG emissions should be reduced by 50 to 80% by 2050 (Change, 2007). In the current circumstances, 80% of primary energy consumption is fulfilled by fossil fuels, of which 58% alone are consumed by the transportation sector (Nam *et al.*, 2011; Nigam and Singh, 2011). Fossil fuel combustion generates greenhouse gases (GHG),

especially carbon dioxide (CO_2), which leads to global warming (Mohammed *et al.*, 2011). Moreover, GHG contribute many negative effects like rising sea levels, acid rain and biodiversity losses (Beer *et al.*, 2002; Howarth *et al.*, 2011). Hence, it is necessary to furnish processes, methods and applications suitable for returning CO_2 to prior lower levels. Three means of reducing the CO_2 amount in the atmosphere include: (i) direct CO_2 emission reduction; (ii) CO_2 capture and storage (CCS); and (iii) CO_2 consumption (Hurst *et al.*, 2012; Windle and Perutz, 2012). CO_2 emission reduction appears unrealistic owing to the current human lifestyle and evolving fossil fuel utilization. CCS technology potential is controllable on account of environmental leakage hazards as well as the energy utilized to compress and transport fuel. Solar energy is the most exploitable of all renewable resources, as it provides the most energy on Earth. Harvesting sunlight to mitigate environmental concerns is a favorable approach besides one of the fundamental aims for global development sustainability (Sato *et al.*, 2015). Nonetheless, amongst all the existing technologies to reduce CO_2 emissions, photocatalysis has been extensively applied to tackle this problem as well as to provide sufficient energy for the future. Nonetheless, amongst all existing technologies to reduce CO_2 emissions, photocatalysis has been extensively applied to tackle this problem as well as to provide sufficient energy for the future. The photocatalytic CO_2 reduction technique is very effective, since it does not require extra energy nor has a negative environmental impact. Due to the low cost involved, utilizing the abundant, free sunlight in converting CO_2 into different products comprising carbon is another excellent approach. This research field has started attracted interest with Fujishima and Honda's work in 1972 . Progress in research has witnessed nanotechnology advances, notably synthesizing nanomaterials with varying structures and morphologies. The most current means involves utilizing noble metals like Au or Ag with surface plasmon resonance (SPR) to improve TiO_2 photocatalytic efficiency (An *et al.*, 2012; Li *et al.*, 2012a). The current study presents a review of the fundamental principles of CO_2 photocatalysis and photocatalytic CO_2 reduction in the presence of CH_4 using a plasmonic photocatalyst and sunlight irradiation. The photocatalytic efficiency measures are discussed as well.

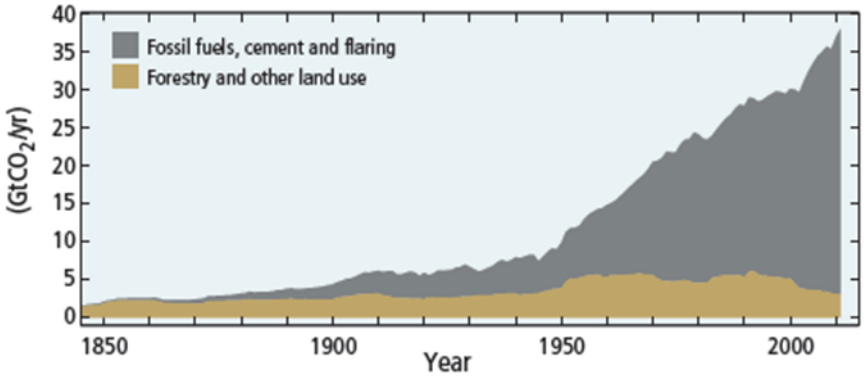

Figure 1.3 Global anthropogenic CO_2 emissions (Allen *et al.*, 2014)

1.2 Fundamentals of Photocatalysis

The word "photocatalysis" is of Greek origin and comprises two sections: photo (phos: light) and catalysis (katalyo: break apart, decompose) (Kondarides, 2005). Photocatalysis is defined as the change in the rate of a photonic reaction by means of a catalyst in the presence of either UV or visible light to boost the reaction. In such reactions, upon impact of the high energy photons onto the semiconductor surface, the electrons in the valence bands obtain enough energy to move to higher-energy conduction bands. The energy required is called the band gap energy and it is the difference between the energies of the valence and conduction bands. The conduction bands are unoccupied, hence the entering electrons move freely between molecules, creating positively charged holes. The negatively charged electrons and positively charged holes can each start a series of reactions like contaminant degradation (Demeestere *et al.*, 2007). The valence band (VB) is the highest electron energy range at which all energy levels are filled by electrons, while the conduction band (CB) is the lowest range of vacant electronic states, which is unfilled by electrons. However, the VB redox potential must be more positive than that of the adsorbates. Similarly, CB electrons must have more negative redox potential to reduce the adsorbate species. On the other hand, it is possible for e^-/h^+ to recombine in the semiconductor catalyst volume (called volume recombination) to create unproductive products or heat (Sachs *et al.*, 2016). Fujishima (1972) initially studied photocatalysis and discovered the photocatalytic activity of TiO_2 electrodes in the decomposition of

water into hydrogen and oxygen. This is the beginning of a new field of heterogeneous photocatalysis.

1.3 Fundamental Role of Photocatalysis in Reducing GHG

Over the past few decades, photocatalytic reactions have had an significant role in various fields, such as water splitting, environmental pollution control, water and air purification, self-cleaning surfaces, and CO_2 concentration reduction, the last of which is deemed the most important concern regarding global warming and also overcoming human health problems (Bourikas *et al.*, 2005). Greenhouse gases are the main reason for global warming, which is now the main concern worldwide. Fossil fuels are dramatically depleting globally every year owing to the high energy demand of humans. Consequently, to fulfill energy demands and prevent global heating, numerous strategies have been proposed by researchers, scientists and investigators over the past four decades or more. Therefore, CO_2 reduction into valuable compounds or chemicals is the most widely utilized technology to overcome these issues and provide future energy simultaneously. Previous work on photocatalysis by Honda-Fujishima has sparked an abundance of research on exploring new ways to apply CO_2 reduction, such as self-cleaning coatings (Blossey, 2003; Xin *et al.*, 2016), electrochronic display devices (Liu *et al.*, 2013), electrochemical CO_2 reduction (Wang *et al.*, 2015b) and photovoltaic (Schreier *et al.*, 2015). Moreover, biological reduction by plants (Zang *et al.*, 2015), thermal CO_2 photocatalytic reduction (Marxer *et al.*, 2015) and photoelectrochemical reduction of CO_2 reported by Halmann *et al.* (1978) have been carried out using electrochemical cells. Unfortunately, electrochemical cells for CO_2 conversion have disadvantages owing to their very slow kinetics as well as very high energy intensity (Cole and Bocarsly, 2010). In addition to the above-mentioned methods, photocatalysis technology has been extensively studied for CO_2 reduction into valuable fuel products owing to its advantages including low input energy consumption and renewable energy use (Usubharatana *et al.*, 2006; Wen *et al.*, 2015). Photocatalysts can be solids or in suspension and can stimulate reactions in the presence of a light source like UV or solar light without the catalyst itself being consumed. However, several photocatalysts, such as TiO_2, ZrO_2, CdS,

ZnO, ZnS, SiC, CeO_2 and Fe_2O_3 can often be used for the photoreduction of GHG and photo-excited electron reduction of CO_2 with other compound reductants to create energy-bearing products like carbon monoxide, methanol, ethylene, ethane, acetic acid, etc. (Hernández-Alonso *et al.*, 2009). Amongst all abovementioned photocatalysts, titanium dioxide is the most extensively investigated due to its unique properties. Owing to its high levels of photoconductivity, ready availability, environmentally friendliness, non-toxicity, low cost and high stability, titanium dioxide is the most frequently employed semiconductor in heterogeneous photocatalytic reactions (Gupta and Tripathi, 2011; Zúñiga-Benítez and Peñuela, 2016). Of the semiconductors mentioned above, TiO_2 exhibits higher photocatalytic activity. ZnO and CdS have lower photoactivity than Titania but pose the disadvantage of releasing Cd^{2+} and Zn^{2+} ions into the solution (Piumetti *et al.*, 2014).

1.4 Problem Statement

CO_2 and CH_4, respectively, are the most significant components of greenhouse gases. The emission of GHG into the environment causes a lot of problems regarding safety and the health of the environment itself. The key CO_2 emission source is the burning of fossil fuels, such as oil, natural gas, coal, etc., which not only accelerate the greenhouse effect but are generated by human activity, at about 37 billion tons of CO_2 emissions each year, about 30 gigatons (Gt) of this being from energy-related emissions. However, burning 1 t of carbon from fossil fuels releases more than 3.5 t of carbon dioxide (Jiang *et al.*, 2010). Therefore, environmental pollution due to fossil fuel use is the main reason for the increasing application of new clean energy sources like sunlight. As a result, means of transforming natural gas into useful fuels have been deliberated. Among these methods, which is also the focus of this study, is the photocatalytic reduction of methane and carbon dioxide into high-value products. The major challenges addressed in this study are:

- The reaction between CH_4 and CO_2 is an uphill type reaction due to the conversion of CO_2 and CH_4 into hydrocarbon fuels in a two-step process. This process requires higher input energy, which exacerbates greenhouse

gas emissions, leading to uneconomical as well as environmentally unfriendly processes.

- The simultaneous conversion of CO_2 and CH_4 is considered a perfect redox reaction.
- Photocatalysis processes encounter low quantum efficiencies using traditional TiO_2 photocatalysts, which is the primary limitation of using sunlight energy. For instance, traditional photocatalysts almost exclusively focus on TiO_2-based semiconductors that can access only UV light (< 4% sunlight) and thus cannot take advantage of visible light (400-800nm wavelengths). Visible light constitutes approximately 43% of solar energy.

In this research, a new photocatalytic conversion of CO_2 into materials of higher value is attempted, such that the reaction can occur in the visible region for economic affordability. Plasmonic photocatalysis has recently facilitated rapid progress in amending photocatalytic efficiency under visible light irradiation, raising the prospect of utilizing sunlight for energy and environmental applications, such as wastewater treatment, water splitting and carbon dioxide reduction. Plasmonic photocatalysis is done utilizing noble metal nanoparticles dispersed in semiconductor photocatalyst and has two prominent features: the Schottky junction and local surface plasmonic resonance (LSPR). The novelty of this study is summarized as follows. By harvesting visible light, novel plasmonic photocatalysts offer potential solutions for some of the main drawbacks in this reduction process. Hence, stainless steel webnet was selected as a photocatalyst support due to its large surface area that provides more active sites for TiO_2 deposition than general supports. This highlights the activities of the plasmonic photocatalysts reduction of CO_2 with CH_4 under visible light irradiation at ambient temperature and low pressure.

1.5 Research Hypothesis

The focus of the present study is on designing a visible-light-active plasmonic photocatalyst to enhance visible light absorption and reduce the electron-hole recombination rate, which can result in high photocatalytic efficiency as well as the

conversion of stable CO_2 molecules in the presence of CH_4 into other value-added chemicals. Accordingly, the catalyst nanoparticles and best reactor designed can significantly contribute to the efficiency of photocatalytic reactions. This research is different from several other studies in using plasmonic photocatalyst construction to benefit from sunlight. For this purpose, the following assumptions are made:

I. Semiconductors are especially valuable as photocatalysts due to a combination of their electronic structure, light absorption, charge transport property and excited-state lifetime characteristics. Consequently, titanium dioxide nanoparticles can facilitate solving problems of photocatalysis and help improve photocatalytic activity and selectivity. In addition, smaller particles result in a lower probability of recombination.
II. With intensive light absorption and charge-separation efficiency, plasmonic photocatalysts seem encouraging for mitigating future energy and environmental concerns. Plasmonic nanostructures can drive direct photocatalysis with visible photons, where the nanostructures act as the light absorbers and catalytic-active sites. Plasmonic photocatalysts have been synthesized successfully by modifying TiO_2 nanoparticles with noble metal nanoparticles (NPs) via simple impregnation. Ag nanoparticle sensitizers display a strong photoelectrochemical response in the visible-light region (400−800 nm) due to their surface plasmon resonance.
III. Higher CO_2 and CH_4 reduction and improved photocatalytic activity under UV-visible light irradiation is possible by introducing immobilized Ag/TiO_2 nanoparticles coated on webnet stainless steel. The stainless steel webnet is a photocatalyst support of choice owing to the extensive surface area, which offers more active sites for TiO_2 deposition than common supports. It also enables optimum ventilation for transient gases. Large surface areas may thus greatly improve the photoconversion of CH_4 and CO_2 into high-value products.

Attaining novel multi-phase photocatalysts with heterojunctions is supported by basic knowledge, such as the theory of the structure of atoms and photoelectrochemistry knowledge. The investigation of highly-active visible-light-driven photocatalysts relies on exploring synthesis methods modified with various

conditions, which results in highly-active photocatalysis in terms of CO_2 reduction in the presence of CH_4.

1.6 Research Objectives

The main aim of this work is to reduce the greenhouse gases (CO_2 and CH_4) by applying plasmonic photocatalysis technology under UV-visible light irradiation. For this aim, the following specific objectives of the research are:

1. To synthesize and characterize Ag/TiO_2 NP supported on stainless steel webnet.
2. To evaluate the effect of various process parameters on photocatalytic reduction of CO_2 and CH_4.
3. To determine the optimum reaction condition for higher conversion of CO_2 and CH_4 using response surface methodology (RSM).
4. To study the kinetic and reaction rate parameters of photoreduction over the catalyst.

The principal contribution of this project to research lies in the development of visible-light-driven photocatalysts with enhanced photocatalytic activity for CO_2 reduction in ambient temperature.

1.7 Research Scope

The photocatalytic reduction of pollutants is a traditional means with a long history. At the moment, nano titania is the most widely explored photocatalyst due to its non-toxicity, low cost and high stability, although it cannot absorb light in the visible region of the solar spectrum. Accordingly, the main disadvantage of TiO_2 in applications for this purpose is its low product yield. As a result, numerous methods have been proposed in literature for the development of visible-light-active TiO_2 with high photocatalytic efficiency, such as noble metal loading. In this study, Ag/TiO_2 is

coated on a mesh webnet by the simple and efficient dip coating method. This can improve the overall photocatalysis of semiconductors under UV-visible illumination as well as noble metal nanoparticles combined with semiconductors in order to enhance the charge separation of photogenerated electron-hole pairs. In addition, the stainless steel webnet is an excellent substrate material due to its large surface area that provides more active sites for TiO_2 deposition.

Nanocatalyst characterization of samples is conducted using XRD, FE-SEM, EDX, TEM, FTIR, BET, Raman, TPD-CO_2, PL and UV-Vis spectrophotometry to investigate the purity, crystallography, surface morphology, mesoporosity, pore size distribution, pore value and optical properties of catalysts.

A batch-type stainless steel cube reactor in gas phase is used with a quartz window at the top. The lamp is positioned so as to irradiate the catalyst surface at the top of the reactor. The light source utilized is a 500W high pressure Xenon lamp with 320-700 nm irradiation operated by a high voltage power supply. Xenon lamps are widely used for sun simulation. Afterwards, a reaction with gas feed containing CH_4, CO_2 and N_2 is applied, where the feed ratio values influence selectivity for the desired product formation.

In this study, an attempt is made to determine the functional relationship between four operating parameters, including irradiation time, feed ratio, catalyst loading amount and stainless steel mesh size, based on Response Surface Methodology (RSM) in conjunction with the Box-Behnken design. To generate the design of experiments (DOE), statistical analysis is employed and a regression model is created using STATISTICA software. Optimization is also done for the CO_2 and CH_4 conversion responses.

The Langmuir-Hinshelwood analysis is the most commonly employed kinetic expression, which explains the kinetics of heterogeneous catalytic processes. The reaction mechanism and kinetic model were developed to determine the key parameters in CO_2 and CH_4 reduction applications.

The focus of our research is to design efficient TiO_2-based photocatalysts to reduce the concentration of GHG. The strategy is to develop and improve the photocatalytic performance of TiO_2 as mentioned above. The titania nanoparticles (TNPs) are combined with noble metal NPs, small band gap semiconductors, and plasmonic metal to significantly enhance the visible-light region absorption, charge transfer efficiency and surface area. This study presents an encouraging technique of developing SPR effect-enhanced photocatalysis, with potentially intense implications for solar light utilization in future.

1.8 Organization of Thesis

This thesis consists of seven chapters.

Chapter 1: Introduction; a general overview and discussion related to the research is provided and problem statement, research hypothesis, objectives and scope of this study are defined.

Chapter 2: Literature Review; gives a general overview on TNP structures, a literature review of fabrication methods of TNP, and their application.

Chapter 3: Research Methodology; the general description of research methodology and detailed experimental strategies are discussed.

Chapter 4: Characterization of Plasmonic Nanocatalysts; deliberated the characterizations of nanocatalysts and catalysts coated over the stainless steel mesh.

Chapter 5: Plasmonic Photocatalyst Activity; the description about photoreduction of CO_2 in the presence of CH_4 over Ag/TiO_2 under UV-visible light irradiation.

Chapter 6: Optimization and Kinetic Study; finding the optimal reaction conditions to highest conversion of CO_2 and CH_4 by RSM method as well as description of kinetics parameter.

Chapter 7: Conclusions and Recommendations; contains the overall conclusions of this study and recommendations for the future work.

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