PHOTOCATALYTIC BIREFORMING OF METHANE OVER SILVER-LANTHANUM MODIFIED GRAPHITIC CARBON NITRIDE WITH TITANIA NANOCOMPOSITE IN MONOLITH PHOTOREACTOR

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This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Photocatalytic conversion of carbon dioxide (CO_2) and methane (CH_4) offers a solution of greenhouse gas mitigation with alternative energy supply. The objective of this study is to design and fabricate photoreactor system and to synthesize silver (Ag) and lanthanum (La) modified protonated carbon nitride (pCN) coupled titanium dioxide (TiO_2) photocatalysts for enhanced photocatalytic CO_2 reduction with CH_4 in the presence of water to fuels. The ternary Ag-La/pCN-TiO_2 composite catalysts were synthesized through sonicated assisted hydrothermal and sol-gel methods. The performance of nanomaterials was investigated using photocatalytic bireforming of methane (BRM), dry reforming of methane (DRM), steam reforming of methane and steam reforming of carbon dioxide in a fixed-bed and monolith photoreactors under UV and visible light irradiations. Ag/La-loaded protonated carbon nitride nanotubes (pCNNT) produced both carbon monoxide (486 µmol g-cat^{-1} h^{-1}) and hydrogen (79 µmol g-cat^{-1} h^{-1}) under visible light irradiations, while productivity was highest in BRM process, which was further improved in a monolith photoreactor with CO and H_2 production rate of 770 and 891 µmol g-cat^{-1} h^{-1}, respectively. Furthermore, using pCN-TiO_2 composite loaded with La, higher amount of CO was obtained, while production of H_2 had increased with Ag-loading. More importantly, a remarkable improvement in productivity of both CO and H_2 with H_2/CO ratio greater than one was obtained using Ag-La co-loaded pCN-TiO_2 composite catalyst. The highest CO and H_2 production rate of 2105 and 2387 µmol g-cat^{-1} h^{-1}, respectively, were obtained using BRM process in a monolith photoreactor. The performance of monolith photoreactor was 1.4 and 3.2 fold higher for CO and H_2 rich synthesis gas (syngas) production than using fixed-bed reactor over the composite catalyst under UV-light irradiations. The reaction mechanism based on Z-scheme system for DRM and BRM was successfully developed under UV light irradiation, while direct electron transfer was observed under visible light irradiations. The quantum efficiency of 4.07 % and 4.624 % was achieved for CO and H_2 production, respectively in a monolith photoreactor, while it was only 1.144 % and 0.548 % in a fixed-bed photoreactor during BRM under UV-light irradiations. Among the operating parameters, feed ratio was the influential parameter to maximize yield and selectivity. The stability test revealed prolonged life and reusability of Ag-La/pCN-TiO_2 composite photocatalyst in three cyclic runs. The Langmuir-Hinshelwood model confirms surface reactions due to efficient sorption process in a monolith photoreactor over composite catalysts. In conclusion, Ag-La loaded pCN-TiO_2 composite catalyst and monolith photoreactor via BRM provided an ideal system to get hydrogen enrich syngas production for renewable fuels productions.

ABSTRAK

Penukaran fotobermangkin karbon dioksida (CO_2) dan metana (CH_4) menawarkan penyelesaian pengurangan gas rumah hijau dengan bekalan tenaga alternatif. Objektif kajian ini adalah untuk merekabentuk dan menghasilkan sistem fotoreaktor dan untuk mengsintesis fotomangkin karbon nitrida berproton (pCN) gandingan titanium dioksida (TiO_2) terubahsuai dengan perak (Ag) dan lantanum (La) untuk meningkatkan penurunan CO_2 fotobermangkin dengan CH_4 dalam kehadiran air kepada bahan api. Pemangkin komposit tetiga Ag-La/pCN-TiO_2 disintesis melalui kaedah hidrotermal dan sol-gel dibantu dengan sonikasi. Prestasi nanobahan dikaji dengan menggunakan dwipengubahan fotomangkin metana (BRM), pengubahan kering metana (DRM), pengubahan wap metana dan pengubahan wap karbon dioksida dalam fotoreaktor lapisan tetap dan monolit di bawah penyinaran cahaya UV dan nampak. Nanotiub karbon nitrida berproton termuat Ag/La (pCNNT) menghasilkan kedua-dua karbon monoksida (486 µmol g-cat^{-1} h^{-1}) dan hidrogen (79 µmol g-cat^{-1} h^{-1}) di bawah penyinaran cahaya nampak, sementara produktiviti tertinggi dalam proses BRM, yang bertambah baik dalam fotoreaktor monolit dengan kadar penghasilan CO dan H_2 masing-masing sebanyak 770 dan 891 µmol g-cat^{-1} h^{-1}. Selain itu, dengan menggunakan komposit pCN-TiO_2 termuat dengan La, jumlah CO yang lebih tinggi diperoleh, manakala penghasilan H_2 meningkat dengan pemuatan Ag. Lebih penting lagi, peningkatan produktiviti kedua-dua CO dan H_2 dengan nisbah H_2/CO lebih besar daripada satu diperoleh dengan menggunakan pemangkin komposit pCN-TiO_2 yang dimuatkan bersama Ag-La. Kadar penghasilan CO dan H_2 tertinggi masing-masing sebanyak 2105 dan 2387 µmol g-cat^{-1} h^{-1} diperoleh dengan menggunakan proses BRM dalam fotoreaktor monolit. Prestasi fotoreaktor monolit adalah 1.4 dan 3.2 kali ganda lebih tinggi bagi penghasilan gas sintesis yang kaya dengan CO dan H_2 (singas) berbanding dengan menggunakan reaktor lapisan tetap terhadap mangkin komposit di bawah penyinaran cahaya UV. Mekanisme tindak balas berasaskan sistem skema Z untuk DRM dan BRM berjaya dibangunkan di bawah penyinaran cahaya UV, manakala pemindahan elektron langsung diperhatikan di bawah penyinaran cahaya nampak. Kecekapan kuantum 4.07% dan 4.624% dicapai untuk pengeluaran CO dan H_2, masing-masing di dalam fotoreaktor monolit, manakala hanya 1.144% dan 0.548% di dalam fotoreaktor lapisan tetap semasa BRM di bawah penyinaran cahaya UV. Antara parameter operasi, nisbah suapan adalah parameter berpengaruh untuk memaksimumkan hasil dan kepemilihan. Ujian kestabilan menunjukkan hayat berpanjangan dan kebolehgunaan semula fotomangkin komposit Ag-La/pCN-TiO_2 dalam tiga kitaran larian. Model Langmuir-Hinshelwood mengesahkan tindak balas permukaan disebabkan oleh proses penyerapan yang cekap di dalam fotoreaktor monolit melalui mangkin komposit. Kesimpulannya, mangkin komposit pCN-TiO_2 yang dimuatkan Ag-La dan fotoreaktor monolit melalui BRM menyediakan sistem yang ideal untuk mendapatkan singas diperkaya hidrogen untuk penghasilan bahan api yang boleh diperbaharu.

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LIST OF ABBREVIATIONS

BRM	-	Bireforming of Methane
CPSI	-	Channels Per Square Inch
CB	-	Conductance Band
DRM	-	Dry Reforming of Methane
F-T	-	Fischer-Tropsch
GHG	-	Greenhouse gas
L-H	-	Langmuir-Hinshelwood
LSPR	-	Localized Surface Plasmon Resonance
MFC	-	Mass flow controller
NHE	-	Normal Hydrogen Electrode
PL	-	Photoluminescence
pCNNT	-	Protonated Carbon Nitrides Nanotubes
pCN	-	Protonated Carbon Nitride
QE	-	Quantum Efficiency
SRM	-	Steam Reforming of Methane
VB	-	Valence Band

LIST OF SYMBOLS

α	-	Absorption coefficient
β	-	Full peak width at half maximum
c	-	Speed of light
d_h	-	Channel size
D	-	Average particle size
E_F	-	Fermi level
e-	-	Electron
E_{bg}	-	Energy band gap
E	-	Activation energy
E_p	-	Energy of photon
f	-	Photon flux
h	-	Plank constant
ΔH	-	Change in enthalpy of reaction (kJ/mole)
h^+	-	Hole
H	-	Heat of reaction
I	-	Irradiance
L	-	Thickness of crystallite (nm)
λ	-	X-ray wavelength
θ	-	Braggs angle

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CHAPTER 1

INTRODUCTION

1.1 Background Overview

Global warming effects due to greenhouse gases, primarily carbon dioxide (CO_2) and methane (CH_4) emitted due to fossil fuel combustion and human activities are prevalent [1]. The emission reduction of CO_2 for cleaner environment can be categorized into three routes which include direct reduction of CO_2 emission from the source [2], CO_2 capture and storage (CCS) and utilization of CO_2. The direct CO_2 emission at the source can be reduced using renewable energy resources that produces lesser CO_2 [3], but these energy sources are limited compared to fossil fuels [4]. CO_2 capture and storage is a technology that is being developed to allow CO_2 emissions from fossil fuel, capture at large point sources to be transported to safe geological storage, rather than being emitted to the atmosphere [5]. CCS disadvantage is the extra cost to transport and injection to the geological storage. Besides, due to industrialization integrated with daily human activities caused the increase of fossil fuels combustion; thus mitigating CO_2 emission and/or storage for sustainable development is unachievable [6]. Therefore, utilization of CO_2 to produce chemicals and fuels is the growing concern in recent years [7].

Among the available CO_2 utilization approaches, the most widely employed technologies are thermal and plasma processes. In thermal process, CO_2 can be converted through an endothermic process by providing an input energy at elevated temperature. However, higher temperature makes this process expensive and has adverse effect on the catalyst stability, while coke produced ultimately deactivates the catalyst [8]. On the other hand, plasma technology for dry reforming of methane is considered better alternatives compared to thermal process. The plasma reforming has advantages of high conversion because reactions are conducted by electron induced chemistry. However, production of large amounts of coke during dry reforming of

methane in plasma reactor is a great challenge. In addition, higher input energy is required to generate plasma, which make this process un-economical [9-11].

In recent innovations, phototechnology has gained much attention because it works in the presence of light irradiations. Using photocatalysis, CO_2 reforming of CH_4 would be possible at normal temperature and atmospheric pressure [12]. The requirement of input energy as like endothermic process can be provided through harvesting solar energy. More importantly, catalyst can be used with prolonged stability due to mild operating conditions, while economical production of chemicals and fuels.

1.2 Photocatalytic CO_2 Reforming of CH_4

Photocatalytic reduction of CO_2 seems a potential technology to produce chemicals and fuels at normal operating conditions with the help of light irradiations. During the past three decades, photocatalytic reduction of CO_2 over various semiconductor materials has been investigated by many researchers and products reported were carbon monoxide (CO), methane (CH_4), methanol (CH_3OH), formic acid (HCOOH) and acetic acid (CH_3COOH) as discussed in Equations (1.1) to (1.5) [13-16].

$$CO_2 + 2H^+ + 2e^- \xrightarrow{hv, catalyst, gas\ phase} CO + H_2O \quad (1.1)$$

$$CO_2 + 2H^+ + 2e^- \xrightarrow{hv, catalyst, slurry} HCOOH \quad (1.2)$$

$$CO_2 + 6H^+ + 6e^- \xrightarrow{hv, catalyst, slurry/gas} CH_3OH + H_2O \quad (1.3)$$

$$CO_2 + 8H^+ + 8e^- \xrightarrow{hv, catalyst, gas\ phase} CH_4 + 2H_2O \quad (1.4)$$

$$2CO_2 + 8H^+ + 8e^- \xrightarrow{hv, catalyst, slurry} CH_3COOH + 2H_2O \quad (1.5)$$

Since 1980s, water as a reductant for the reduction of CO_2 in a gas phase and slurry system, has attracted considerable interest with diversity of products (e.g., CO,

CH_4, H_2, CH_3OH, HCOOH and HCHO) [13-16]. Using gas phase system, CO_2 with water can be converted to CO, CH_4 and CH_3OH as the potential products. However, slurry system promoted the production of CH_3OH, HCHO and CHOOH during CO_2 reduction with H_2O [17]. In this perspective, production of CH_4 from photo-reduction of CO_2 with water vapours over Fe/TiO_2 [18], photo-reduction of CO_2 with H_2O to liquid products (CH_3OH, HCHO) over CeO/TiO_2 [19], use of $Ag\text{-}MgO/TiO_2$ for the production of CH_4 from CO_2 and water in gas phase system [20], Fe-doped CeO for CO and CH_4 production from CO_2 and water vapours [21], production of CO from CO_2-water vapours over Ag/CdS [22], Ag/TiO_2 nanorods [23], $g\text{-}C_3N_4/Ag/TiO_2$ composite catalyst for the production of CO and CH_4 from CO_2-water [24], production of CO from CO_2-water using $g\text{-}C_3N_4/N/TiO_2$ catalyst [25] and $g\text{-}C_3N_4/Cu/TiO_2$ for the production of CH_3OH, HCHO and HCOOH from CO_2 in slurry system [26], have been reported.

Although, different types of photocatalysts with appreciable improvement in CO_2 reduction to fuels has been succeeded by numerous researchers, but main challenge is diversity of products distribution. In addition, research on utilization of both greenhouse gases (CO_2 and CH_4) is still relevant. CH_4 is emitting from gas supply chain [27], landfill [28] and industries, is a severe challenge for the future. Therefore, recycling both greenhouse gases (CO_2 and CH_4) to valuable chemicals and fuels by reforming deems an attractive pathway for a cleaner environment. CO_2 reforming is a method of producing synthesis gas (syngas), a mixture of CO and H_2, from the mixture of CO_2 and hydrocarbons, in particular, methane. Conventionally, syngas is produced via dry reforming of methane. The reforming of CO_2 and CH_4 is a challenging task as both are stable molecules, while reforming of these two molecules to syngas is an endothermic process that demands excessive supply of energy [29, 30]. However, it is a main raw material in the production of liquid fuels. Besides, syngas (H_2/CO) ratio for the production of liquid fuels has great importance, e.g., a ratio of H_2/CO of 2 would be required in methanol synthesis process.

Methane can be converted into syngas through different reforming technologies such as steam reforming of methane (SRM) as shown in Equation (1.6). CO_2 can also be utilized with CH_4 for the production of syngas through catalytic CO_2

and CH_4 reforming or dry reforming of methane (DRM) as explained in Equation (1.7) [31]. DRM offers advantages such as mitigating both greenhouse gases, and direct production of syngas [32]. However, DRM operates under higher temperature via thermal reforming is prone to coking and reduces catalyst stability [33].

$$\begin{aligned} &CH_4 + H_2O \longrightarrow CO + 3H_2 \\ &\Delta H_{298K} = +206\ \text{kJ/mol} \\ &\Delta G_{298K} = +142\,\text{kJ/mol} \end{aligned} \tag{1.6}$$

$$\begin{aligned} &CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \\ &\Delta H_{298K} = +247\ \text{kJ/mol} \\ &\Delta G_{298K} = +170\,\text{kJ/mol} \end{aligned} \tag{1.7}$$

Combination of SRM and DRM also known as bireforming of methane (BRM) could be a promising approach and interesting pathway for the production of H_2 enriched syngas as explained in Equation (1.8) [34]. BRM has advantage over SRM and DRM for producing hydrogen with a stoichiometric H_2/CO ratio of 2, a more favourable composition for the production of liquid fuels via Fischer-Tropsch Synthesis (FTS) [35]. Although, BRM is an attractive approach compared to DRM, yet it also requires larger input energy due to endothermic process [36].

$$\begin{aligned} &3CH_4 + CO_2 + 2H_2O \longrightarrow 4CO + 8H_2 \\ &\Delta H_{298K} = +220\ \text{kJ/mol} \\ &\Delta G_{298K} = +151\,\text{kJ/mol} \end{aligned} \tag{1.8}$$

With the help of phototechnology, reforming processes can be conducted at normal temperature and atmospheric pressure. However, there are limited reports available on photocatalytic CO_2 reduction with CH_4 through phototechnology. Recently, photocatalytic CO_2 reforming of CH_4 to fuels over different semiconductor photocatalysts has been reported [37, 38]. In one of the earlier studies, Shi et al. [39] reported photocatalytic CO_2 reduction with CH_4 over Cu/CdS modified TiO_2/SiO_2 photocatalyst in a fixed-bed photoreactor operating at high temperature. Products obtained were C_2H_6, CH_3COOH, CH_3COCH_3 and CO. ZrO_2 photocatalyst was employed for CO_2-CH_4 reduction under UV-light with the production of CO and H_2

as the main products [40]. Similarly, CO and H_2 were produced during CO_2 reduction with CH_4 over Pt-loaded TiO_2 and Au/Rh loaded TNTs catalyst, respectively [41]. However, literature on photocatalytic CO_2 reduction with CH_4 in the presence of H_2O via BRM is not available. Besides, ubiquitous TiO_2 is mainly employed as a photo-catalyst in CO_2 reforming of CH_4, but the production rate was not much appreciable. Lower TiO_2 photoactivity attributing to poor CO_2 adsorption due to acid nature and fast photogenerated charges recombination rate.

Significant research has been conducted on developing efficient photocatalysts, while the use of basic oxide in TiO_2 is considered as one prospect to promote CO_2 adsorption. In recent years, rare-earth metals are typically investigated for the modification of TiO_2 structure to enable the increment of surface oxygen vacancies [42]. Lanthanum (La), due to the unique electronic configuration and spectral characteristics,), is considered as the best dopant for modifying crystal structure, optical properties and surface adsorption of TiO_2 [43, 44]. Li et al., [45] reported the use of La as an efficient metal for selective photocatalytic CO_2 reduction with H_2O to CH_4 under UV-light. The enhanced and selective photoactivity of La/TiO_2 photocatalyst was due to higher CO_2 adsorption because of its surface basicity with proficient charge separation. Similarly, silver (Ag) metal is gaining large interest due to its appropriate work function (W_s) for photocatalytic applications [46, 47]. Many research articles reported the use of Ag based semiconductors for selective CO_2 photoreduction during photocatalytic CO_2 reduction with H_2O under UV and visible light irradiations [48-52].

Recently, graphitic carbon nitride (g-C_3N_4) semiconductor is considered very promising for CO_2 reduction applications. This is because of its merits of low-cost preparation, high chemical stability and possessing appropriate electronic structure with medium band gap energy (2.70 eV) [53, 54]. Nevertheless, photoactivity of the pure g-C_3N_4 is still limited due to fast charges recombination rate [55]. Many attempts have been employed to increase the performance of g-C_3N_4 such as surface charge modification, designating an appropriate textural porosity, metal doping, non-metal doping and coupling with other semiconductors [26, 56]. Ong and co-workers reported the surface charge modification of g-C_3N_4 via protonation with enhanced photo-

activity for CO_2 reduction to CH_4 [57]. In another work, g-C_3N_4 loaded with Pt for enhanced CH_4 production during photocatalytic CO_2 reduction has been reported [58]. CeO_2 loaded into g-C_3N_4 remarkably enhanced photocatalytic activity for CO_2 reduction by H_2O to CO and CH_4 [59]. Similarly, Ag-loaded-gC_3N_4 has been investigated for selective H_2 production as Ag suppressed the recombination of charge carriers [49, 60].

In the recent development, fabrication of semiconductors heterojunctions or Z-scheme photo-catalysts are considering more significant due to efficient charges separation with the adjustment of band structure for selective CO_2 reduction to fuels. In this perspective, CO_2 photoreduction with H_2O to CH_3OH was tested using g-C_3N_4/Cu/TiO_2 as a photo-catalyst [26]. In another work, indirect Z-scheme BiOI/g-C_3N_4 was investigated for visible light driven CO_2 reduction with H_2O with the production of CO, H_2 and CH_4 [61]. The selective photocatalytic CO_2 reduction with H_2O over g-C_3N_4-N/TiO_2 [62], ZnV_2O_6/g-C_3N_4 [63] and Mg-gC_3N_4 [64] composites have been investigated. Similarly, Ag-loaded g-C_3N_4/TiO_2 for CO_2 photo-reduction by H_2O to fuels was explored [24]. g-C_3N_4 is widely investigated in photocatalytic CO_2 reduction with H_2O, but not for CO_2-CH_4 reaction system via DRM and BRM. The efficiency of g-C_3N_4 can be further improved through surface charge modification via protonation [63]. Besides, development of Ag/La modified Z-scheme g-C_3N_4/TiO_2 composite would be promising for enhanced photocatalytic dry and bireforming of methane.

Upscaling CO_2 reforming of CH_4 system to synthesis gas (CO and H_2) requires stringent criteria for designing the photoreactor system. The choice of reactor is critical since it affects the overall CO_2 reduction efficiency and products selectivity. Almost all photoinduced CO_2-methane reaction systems were conducted in a fixed-bed photoreactor, where catalysts are distributed over the reactor surface. The fixed-bed reactors have limitations: (1) poor light utilization efficiency due to less exposed active surface area; (2) lower adsorption- desorption process due to less contact of gas with catalyst; (3) smaller catalyst loading and (4) less light intensity to stimulate complex nature of CO_2-CH_4 photocatalytic reaction [65]. Therefore, the design of highly

efficient photoreactor for CO_2-CH_4 reduction is crucial to scale up phototechnology from laboratory to commercial level.

More recently, the attention on immobilized photocatalytic systems with enhanced light utilization efficiency has surged [66, 67]. Among the different supports, monolithic substrates are mainly studied because of the unique structure, higher adsorption-desorption process, larger active surface area, more catalyst loading, controlled selectivity and large photonic efficiency [66, 68]. In this perspective, monolith photoreactor found very efficient for photocatalytic CO_2 reduction to CO with enhanced selectivity and yield using H_2O and H_2 reductants over different types of semiconductor materials [48, 69].

The focus of this study is to design and develop structured Ag/La modified g-C_3N_4-TiO_2 nanocomposite for photocatalytic dry and bireforming of methane in a monolith photoreactor. The coupling TiO_2 and g-C_3N_4 will be suitable for Z-scheme photocatalytic reactions under UV-light and direct heterojunction electron transfer under visible light. The modification of g-C_3N_4/TiO_2 with La/Ag metals will develop novel polymeric complexes that would maximize the process efficiency under UV and visible light irradiations. The use of water in dry reforming of methane would be suitable for the production of hydrogen enrich syngas. The monolith photoreactor will maximize the illuminated surface area even at lower light intensity, thus increasing the efficiency of reactor system for CO_2 photo-reduction to hydrogen enrich syngas. The optimization of different operating parameters and kinetic investigation will further improve the system efficiency.

1.3 Problem Statement

The conversion of greenhouse gases i.e., CH_4 and CO_2 to renewable fuels has become a challenge to achieve net-zero carbon cycle for monitoring energy crises and environment pollution. The breaking stable molecules of CH_4 and CO_2 demands higher input energy, while overcoming this barrier through external supply of energy makes

this process uneconomical. The main challenges for the conversions of greenhouses to chemicals and fuels are as follows:

1. Thermal process requires higher input energy to break stable CO_2 and CH_4 molecules. The energy barrier for recycling CO_2 and CH_4 can be resolved using phototechnology, yet limited reports are available on photocatalytic CO_2 reduction with CH_4. The lower production rate during photocatalytic conversion of CO_2 and CH_4 with diversity of products is another barrier in the use of phototechnology;

2. Among the semiconductors, TiO_2 and metal modified TiO_2 photocatalysts have been investigated for CO_2 reforming of CH_4. However, TiO_2 yielded lower photo-activity due to faster charges recombination and inappropriate redox potentials. This urges to find new and highly efficient composite photocatalyst for selectivity DRM process under UV and visible light irradiations. Recently, g-C_3N_4 has been investigated for CO_2 reduction with H_2O applications, however, it has not been reported in DRM and BRM applications;

3. The production of synthesis gas with higher H_2/CO ratio in another challenge in photocatalytic dry reforming of methane process. This is because, during photocatalytic CO_2 reduction with CH_4, diversity of products has been reported;

4. Besides, photoreactors investigated are fixed-bed which have lower quantum efficiency. These reactors are not very efficient due to inefficient light distribution and have minimum surface area for carrying catalytic reactions.

1.4 Research Hypothesis

The lower CO_2 conversion efficiency and production rates through phototechnology can be improved by employing an efficient reducing agent, photocatalyst and photoreactor. Therefore, the followings are the research hypothesis:

1. Although, both CO_2 and CH_4 are very stable molecules, yet CO_2 and CH_4 can be converted to chemicals using phototechnology. The problem of lower TiO_2 photoactivity can be resolved by loading with basic oxide materials, in particular lanthanum (La). Basic oxides would be helpful to improve CO_2 adsorption and will promote charges separation.

2. The use of graphitic carbon nitride (g-C_3N_4) would be promising in photocatalytic CO_2 reduction with CH_4 due to its visible light response, appropriate band structure and low-cost synthesis. The surface charge modification and addition of metals such as Ag and La metals would be promising to improve efficiency and selectivity for synthesis gas production;

3. Coupling g-C_3N_4 with TiO_2 will provide appropriate band structure with efficient charges separation and would enable efficient reduction of CO_2 with CH_4 under UV and visible light irradiations. For this purpose, direct heterojunction of g-C_3N_4/TiO_2 for visible light and Z-scheme g-C_3N_4/TiO_2 nanocomposites would be promising for UV-light applications. The efficiency of composite will be further improved by loading with Ag and La metals, thus would be helpful to improve photoactivity and selectivity;

4. Composition of synthesis gas can be adjusted using different reforming technologies. The lower H_2/CO ratio in synthesis gas during CO_2 reduction with CH_4 can be improved by combining DRM process with steam reforming of methane (SRM). Thus, photocatalytic CO_2 reduction with CH_4 in the presence of H_2O via bireforming of methane (BRM) would be promising to get higher production rate and selectivity;

5. The lower quantum efficiency of photoreactor system because of inefficient light distribution over the catalyst surface is intended to overcome employing monolith photoreactor. The monolith photoreactor will be productive to provide larger illuminated active surface area, higher adsorption-desorption and efficient mass transfer toward the catalyst surface. Higher light distribution and harvesting over the catalyst surface would also be possible utilizing micro-channels, ultimately stimulating higher quantum efficiency toward efficient reduction of CO_2 with CH_4/water system;

6. The effect of different parameters and their optimization would also be helpful to improve production rate and products selectivity. The kinetic study will further provide insights about the photon flux utilization and reaction rate limitations.

1.5 Research Objectives

The objectives of this research are:

(a) To synthesize and characterize Ag/La modified g-C_3N_4-TiO_2 nanocomposite photocatalysts functional under UV and visible light irradiations;

(b) To study the performance of composite nanocatalysts for photocatalytic CO_2 reduction with CH_4/H_2O through dry and bireforming of methane under UV and visible light irradiations;

(c) To compare quantum performance of fixed-bed with a monolith photoreactor for photocatalytic CO_2 reduction with CH_4/H_2O through dry and bireforming of methane;

(d) To investigate effect of process parameters on photocatalytic bireforming of methane over composite photocatalyst in a monolith photoreactor;

(e) To optimize process parameters using response surface methodology and develop kinetic model to determine reaction rate parameters in photocatalytic bireforming of methane.

1.6 Research Scope

This study focused on determining some mechanistic and fundamental problems pertaining to lower CO_2 and CH_4 reduction efficiency and products selectivity. The fabrication of plasmonic and polymeric nanocatalysts with various metals and co-metals loading into pCN and pCN-TiO_2 nanostructures has been

inspected. The effects of operating parameters on CO_2 reduction such as metal-doping levels, feed ratios, and reaction temperature and irradiation times is also deliberated. The performance analysis of a monolith with a fixed-bed photoreactors has been investigated to get higher yield and selectivity. The reaction mechanisms of CO_2 reduction and CH_4/water oxidation and quantum efficiency analysis has been deliberated. The CO_2 reduction efficiency is related to maximize yield of desired products. Therefore, the specific research scope of this study is as follows:

1. The catalysts such as TiO_2, pCN pCN-TiO_2, Ag-La/pCNNT and Ag/La modified pCN-TiO_2 are synthesized using sol-gel and hydrothermal methods to investigate the route of CO_2 reduction with CH_4/H_2O. The optimized materials are supported over the monolith channels using sol-gel dip-coating method. The catalysts are characterized using XRD, SEM, FESEM, HRTEM, BET, XPS, UV-Visible and PL spectroscopy. This was helpful to investigate crystallinity, phase, morphology, surface area, pore size distribution, metals transition states and optical properties.

2. The performance of catalysts for photochemical reduction of CO_2 with CH_4/H_2O is investigated using photocatalytic steam reforming of methane (SRM), photocatalytic dry reforming of methane (DRM) and photocatalytic bireforming of methane (BRM) under UV and visible light irradiations. The role of each catalysts is critically evaluated to understand their impacts on the products yield and selectivity in the presence of different reforming processes and light systems.

3. The photoreactors employed are fixed bed and monolith of multiple channels. The quantum performance of both photoreactors is investigated using different reforming systems (i.e., SRM, DRM and BRM) under UV and visible light irradiations. In a fixed bed, photocatalysts are distributed at the reactor bottom, however, they are coated inside monolith microchannels using sol-gel dip-coating method. The mass flow controllers are employed to adjust feed flow rates and feed ratios in different reaction system. A reflector type 200W Hg lamp is used as a source of UV-light irradiations with intensity 150 mW/cm^2 and wavelength 254 nm. A solar simulator is used as a source of visible light

irradiations with intensity equal to 100 mW/cm^2. More importantly, solar arrays with batteries are installed to provide input electricity for the operation of both photoreactors.

4. The operating parameters investigated are reaction temperature, feed ratios, and monolith geometry and irradiation time. The reaction mechanism is developed to find out key parameters in CO_2 reduction applications for different reforming systems under UV and visible light irradiations.

5. The optimization of process parameters is carried out using response surface methodology (RSM). The kinetic model is developed using Langmuir-Hinshelwood mechanism and rate constants are determined.

1.7 Research Significance

Greenhouse gas CO_2 is efficiently reduced with CH_4 for synthesis gas (CO, H_2) production in the presence of different photo-catalytic systems. The monolith photoreactor performance is very encouraging while the efficiency found was much higher compared to fixed-bed photoreactor. The composite catalysts are highly productive for CO_2 and CH_4 reduction to syngas gas. The several outcomes of this research are described below:

(a) A new route for photocatalytic CO_2 reduction with CH_4 through dry reforming of methane (DRM) and bireforming of methane (BRM) reactions.

(b) Development of microchannel monolith photoreactor system to investigate efficient photocatalytic DRM and BRM for synthesis gas production.

(c) New methods and findings on the synthesis of protonated graphitic carbon nitrides nanotubes and z-scheme composite catalysts.

(d) Low-carbon economy shift through CO_2 recycling.

(e) Alternative solutions to energy crises and global warming.

1.8 Layout of Thesis

The research is focused on the photocatalytic CO_2 reduction with CH_4 through dry reforming of methane and bireforming of methane over Ag or La doped and Ag-La co-doped pCN-TiO_2 composite nanocatalyst in a fixed-bed and continuous mode operation of monolith photoreactor. The development of Ag-La modified pCN-TiO_2 nanocatalyst suitable for efficient CO_2 reduction via DM and BRM with H_2/CO and hydrocarbon fuels has been investigated. The synthesis and characterization of materials, optimization of metals loading, investigation of operating parameters, and evaluation of reactor performances for higher production rate and reaction mechanisms are discussed in different chapters. This thesis consists of eight chapters.

Background of the research and problem at hand, research hypothesis, objectives and scope of this study are discussed in Chapter 1. Chapter 2 presents literature survey pertaining to possible pathways for CO_2 recycling, fundamentals and progress in CO_2 reduction to hydrocarbon fuels, progress in CO_2 reduction with CH_4 over different photo-catalysts, selection of photo-catalysts, and description of photocatalytic reactors. In Chapter 3, general description of research methodology and detailed experimental strategies are discussed. The characterizations of nanocatalysts are discussed in Chapter 4. Performance analysis of metals modified TiO_2 and pCN in a fixed-bed and monolith photoreactor for photocatalytic CO_2 reduction with CH_4/H_2O is presented in Chapter 5. Chapter 6 investigates the photocatalytic CO_2 reduction via BRM over Ag-La modified pCN-TiO_2 catalysts in a microchannel monolith photoreactor under UV-light irradiations. The optimization of process parameters using response surface methdology and kinetic model development has been presented in Chapter 7. Finally, Chapter 8 contains the overall conclusions of this study and recommendations for future work.

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