ZINC VANADIUM OXIDE COUPLED CARBON NITRIDE NANOCOMPOSITE FOR PHOTOCATALYTIC CARBON DIOXIDE REDUCTION TO METHANOL

ABDULLAH SALEM MOHAMMED BAFAQEER

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

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

SEPTEMBER 2019

To my father, mother and family members for their support and sacrifices

ACKNOWLEDGEMENT

I would like to take this opportunity to express my gratitude to Allah S.W.T for His endless mercies, blessings and guidance from birth now and forever.

Firstly, I would love to express my sincere gratitude to my supervisor Dr. Muhammad Tahir for his continuous support throughout my research, for his patience, motivation, enthusiasm, wealth of knowledge and experience. His guidance helped me a lot during my research and the writing of this dissertation. It is a great honor working as your student during my research. I would also like to appreciate my co-supervisor Prof. Dr. Nor Aishah Saidina Amin for her guidance and advices throughout my research. Aside that, I express my sincere appreciation to the Chemical Reaction Engineering Group (CREG) members and other UTM friends for their support and valuable inputs regarding this research.

Last but not least, I owe great thanks to my parents, brothers, sisters, wife and friends that supported me all the way despite the distance. No matter what decision I made, my family was always there for supporting me and pushing me forward and for that no thanks can express my gratitude.

ABSTRACT

Photocatalytic reduction of carbon dioxide (CO_2) with water (H_2O) into solar fuels is considered as a promising strategy to simultaneously address the global energy and environmental issues. The main objective of this study was to design and fabricate photoreactor system and to synthesize Z-scheme assembly of reduced graphene oxide (RGO) and protonated carbon nitride (pCN) based zinc vanadium oxide (ZnV_2O_6) nanocomposite for selective photoreduction of CO_2 to solar fuels. The pure ZnV_2O_6, ZnV_2O_6/RGO, ZnV_2O_6/pCN and ZnV_2O_6/RGO/pCN nanocomposites were synthesized by a single step solvothermal method. The performance of nanocomposite catalysts was investigated in a liquid and gas phase photocatalytic systems under UV and visible light irradiations. The most effective catalyst in liquid phase system was ZnV_2O_6/RGO/pCN which gave a maximum methanol yield of 3726.7 μmol g-cat^{-1} using photoreactor without reflector and 5207.2 μmol g-cat^{-1} using photoreactor with reflector. Performance comparison revealed 1.4 times higher yield rate in photoreactor with reflector compared to photoreactor without reflector. Besides, weight percent ratio, effect of time and stability contributed significantly to enhance reactor performances. Using gas phase system, ZnV_2O_6/RGO/pCN nanocomposite demonstrated excellent photoactivity in the reduction of CO_2 into carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and methanol (CH_3OH) under visible light irradiation. The CO evolution rate as a main product over ZnV_2O_6/RGO/pCN nanocomposite of 3756 μmol g-cat^{-1} was obtained. The quantum efficiency of 14.2 % was achieved for CH_3OH production in a photoreactor with reflector, followed by 10.4 % and 0.25 % in photoreactor without reflector and fixed-bed photoreactor, respectively under visible light irradiation. Finally, Langmuir-Hinshelwood kinetic model was developed to investigate adsorption behaviors and photocatalytic oxidation and reduction process. In conclusion, solar photoreactor with reflector and modified ZnV_2O_6 nanocatalysts could make markedly higher CO_2 reduction to fuels.

ABSTRAK

Penurunan ber fotomangkin karbon dioksida (CO_2) bersama air (H_2O) kepada bahan api solar dianggap sebagai strategi yang baik untuk menangani isu-isu tenaga dan alam sekitar global secara serentak. Objektif utama kajian ini adalah untuk mereka bentuk dan membina sistem fotoreaktor dan untuk mensintesis pemasangan skema Z grafin oksida terturun (RGO) dan nanokomposit zink vanadium oksida (ZnV_2O_6) berasaskan karbon nitrida berproton (pCN) untuk pemilihan fotopenurunan selektif CO_2 kepada bahan api solar. Nanokomposit tulen ZnV_2O_6, ZnV_2O_6/RGO, ZnV_2O_6/pCN dan ZnV_2O_6/RGO/pCN telah disintesis dengan kaedah solvoterma langkah tunggal. Prestasi mangkin nanokomposit telah dikaji di dalam sistem fotomangkin fasa cecair dan fasa gas di bawah penyinaran UV dan cahaya nampak. Mangkin paling berkesan di dalam sistem fasa cecair adalah ZnV_2O_6/RGO/pCN yang memberikan hasil metanol maksimum sebanyak 3726.7 μmol g-cat^{-1} menggunakan fotoreaktor tanpa pemantul (reflektor) dan 5207.2 μmol g-cat^{-1} menggunakan fotoreaktor dengan pemantul. Perbandingan prestasi mendedahkan kadar hasil 1.4 kali lebih tinggi di dalam fotoreaktor dengan pemantul berbanding fotoreaktor tanpa pemantul. Selain itu, nisbah peratus berat, kesan masa dan kestabilan menyumbang kepada peningkatan prestasi reaktor yang ketara. Menggunakan sistem fasa gas, nanokomposit ZnV_2O_6/RGO/pCN menunjukkan aktiviti foto yang cemerlang dalam penurunan CO_2 kepada karbon monoksida (CO), hidrogen (H_2), metana (CH_4) dan metanol CH_3OH di bawah penyinaran cahaya nampak. Kadar pembebasan CO sebagai produk utama bagi nanokomposit ZnV_2O_6/RGO/pCN sebanyak 3756 μmol g-cat^{-1} telah diperoleh. Kecekapan kuantum sebanyak 14.2% telah dicapai untuk penghasilan CH_3OH di dalam fotoreaktor dengan pemantul, diikuti dengan 10.4% dan 0.25% di dalam fotoreaktor tanpa pemantul dan fotoreaktor lapisan tetap, masing-masing di bawah penyinaran cahaya nampak. Akhir sekali, model kinetik Langmuir-Hinshelwood telah dibangunkan untuk menyiasat kelakuan penjerapan dan proses pengoksidaan dan penurunan fotomangkin. Kesimpulannya, fotoreaktor solar dengan pemantul dan nanomangkin ZnV_2O_6 terubahsuai boleh melakukan penurunan CO_2 kepada bahan api yang ketara lebih tinggi.

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LIST OF ABBREVIATIONS

DMF	-	N,N-dimethyl formamide
RGO	-	Reduced graphene oxide
pCN	-	Protonated carbon nitride
ZnV_2O_4	-	Zinc vanadium oxide
g-C_3N_4	-	Graphitic carbon nitride
CO_2	-	Carbon dioxide
GHG	-	Greenhouse gas
VB	-	Valence Band
CB	-	Conduction Band
FESEM	-	Field Emission Scanning Electron Microscopy
BET	-	Braunauer-Emmer-Teller
XRD	-	X-ray Diffraction
PL	-	Photoluminescence
UV/Vis	-	Ultraviolet Visible
XPS	-	X-ray Photoelectron spectroscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
EDX	-	Energy Dispersive Electron Microscope
FID	-	Flame Ionization Detector
GC	-	Gas Chromatography
2D	-	Two-Dimensional
C	-	Concentration

LIST OF SYMBOLS

λ	-	Wavelength
f	-	Photon flux
e^-	-	Electron
h^+	-	Hole
P	-	Pressure
α	-	Alpha
β	-	Beta
θ	-	Theta
Φ	-	phi
E_{bg}	-	Energy band gap
E	-	Activation energy
E_p	-	Energy of photon
h	-	Planks constant
ΔH	-	Change in enthalpy of reaction (KJ/mole)
H	-	Heat of reaction
I	-	Light intensity (mW/cm^2)
I_p	-	Photon Irradiance
k	-	Reaction rate constant
k_1	-	Reduction rate constant
k_2	-	Oxidation rate constant
KJ	-	Kilo Joule
L	-	Length
μm	-	Micrometer
W	-	Watt
T	-	Temperature

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CHAPTER 1

INTRODUCTION

1.1 Problem Background

Climate change because of global warming arising from the emission of greenhouse gas carbon dioxide (CO_2) poses a severe threat to our future [1, 2]. Combustion of fossil fuel is the main source of greenhouse gas emission especially CO_2, which ultimately leads to global warming [3]. Furthermore, greenhouse gases contribute many negative influences such as loss in biodiversity, occurrence of acid rain and increase in sea level [4]. Exploring new energy resources are inevitable to address shortage in fossil fuels supply, continuous increase in energy demand and pressing environmental issues [5]. Recently, many efforts were endorsed to decrease CO_2 emission through pre or post combustions and also capturing and sequestration. However, these processes are energy intensive, thus uneconomical [6].

Using easily available and renewable carbon resource like CO_2 for improvement of carbon-based fuels is imperative for the sustainability, since CO_2 is totally abundant, cheap and green as well as a renewable feedstock [7]. During the last decade, different types of technologies were investigated for CO_2 reforming to carbon-based fuels namely, plasma reforming, thermal reforming and photoreduction [8]. However, the biggest obstacle for establishing industrial processes based on CO_2 is its low energy level. CO_2 is a stable molecule that requires high energy to convert it into fuels. Therefore, technologies pertinent to carbon management, which not only alleviate global temperature, but also meet increasing energy demands economically, are high in the priority list [9]. Recently, photocatalytic CO_2 reduction has gained significant importance toward production of solar fuels like CH_3OH, CO and CH_4 [10-12]. The phototechnology has high potential for reducing CO_2 emission and partly overcoming energy crises [13, 14]. Therefore, the photoreduction of CO_2 utilizing

visible light illuminations could be a potential pathway for the sustainability of the society.

1.2 Photocatalytic Reduction of Carbon Dioxide

Photocatalytic reduction of CO_2 is one of the most promising solutions to both global warming and energy crises, since CO_2 can be reduced to solar fuels at relatively low temperature and atmospheric pressure [15, 16]. In recent innovations, the ubiquitous photocatalysis has gained increasing attention as it can operate at normal operating conditions. During photocatalytic reduction of CO_2 to solar fuels, energy requirement could be provided using sunlight which is a green source of energy. In this technology, stability of catalyst and its performance is affirmed because of mild operating conditions. The photoreduction of CO_2 by using water (H_2O) as reductant are stated in Equations (1.1) - (1.2).

$$CO_2 + 2H_2O \xrightarrow{hv,catalyst} CH_3OH + \frac{3}{2}O_2 \quad (1.1)$$

$$2CO_2 + 2H_2O \xrightarrow{hv,catalyst} CO + CH_4 + \frac{5}{2}O_2 \quad (1.2)$$

When CO_2 reacts with H_2O in a three phase heterogeneous slurry system (gas, liquid and solid), CH_3OH prevailed during photocatalytic CO_2 reduction with H_2O in a slurry system as explained in Equation (1.1). Using two phase heterogeneous system (gas and solid), CO and CH_4 are produced as explained in Equation (1.2). Equation (1.1) - (1.2) revealed renewable fuels such as CH_3OH, CO and CH_4 can be produced in a single step. Hence, these reactions affirmed phototechnology as the most attractive and a future hope for mitigation of greenhouse gas with production of green fuels for sustainable development [14].

Among various semiconductors, the focus has been on graphitic carbon nitride (g-C_3N_4) as a photocatalyst. g-C_3N_4 has been researched excessively over the past decades due to its encouraging advantages including elemental abundance, high chemical and thermal stability, appropriate band gap energy and eco-friendly nature [17]. However, the performance of g-C_3N_4 is still restricted because of its high recombination rate of photo-produced electron and hole pairs [18-21]. The efficiency of g-C_3N_4 can be improved by exfoliation and functionalization. Several efforts were made to promote the efficiency of g-C_3N_4 like doping with metal and non-metal elements [22], engineering approach [23] and coupling with other semiconductors [24-27]. RGO with two-dimensional structure is one of the most promising mediator/modifier due to its excellent electron mobility and higher light absorption [28, 29]. Modification of g-C_3N_4 with RGO has exhibited considerable progress due to it promotes separation of charges. Thus, numerous research efforts were made to improve g-C_3N_4 efficiency such as RGO/protonated g-C_3N_4 [30], RGO/g-C_3N_4 [31], RGO/g-C_3N_4 [32] and g-C_3N_4/GO [33]. Therefore, it is appropriate to develop g-C_3N_4/RGO based semiconductors for enhanced photocatalytic CO_2 reduction applications under solar energy.

In the current development, ternary nanostructures like nanoplates, nanosheets, microspheres and nanorods have gained much attention and exhibited magnificent performances in photo-induced CO_2 reduction and other energy applications [34-36]. Moreover, the construction of Z-scheme photo-induced system has received much attention because of its ideal effectiveness in improving the photo-induced efficiency [37]. Therefore, developing ternary zinc-vanadium oxide nanostructures could enhance both photoactivity and selectivity. Recently, zinc-vanadium oxide (ZnV_2O_4) has gained attention because of its interesting structural changes at low temperatures [38]. Different nanostructures of ZnV_2O_4 have been reported like hollow spheres, clewlike hollow structures, nanosheets, and glomerulus nano/microspheres for various applications [39-41]. However, structured ZnV_xO_y based photo-catalyst has never been reported for photo-induced CO_2 reduction application.

Therefore, it is appropriate to explore ternary ZnV_2O_6 semiconductor for photocatalytic CO_2 reduction applications under solar energy. Combining 2D ZnV_2O_6

nanosheets with rGO/g-C_3N_4 composite would develop indirect Z-scheme heterojunction which may not only increase charges separation performance but also provides good redox potential for selective CO_2 reduction under visible light. Thus, it is extremely desirable to construct g-C_3N_4 modified RGO/ZnV_2O_6 composite to improve photo-induced conversion of CO_2 into fuels under visible light illuminations.

During the last decade, optical fiber reactors have been under investigation for photoreduction of CO_2. The optical fiber reactors fall in the category of efficient photocatalytic reactors. These reactors have been explored for photocatalytic reduction of CO_2, since the exposed surface area to light ratio are larger, delivering light efficiently and uniformly throughout the reactor [42, 43]. However, several disadvantages such as lower adhesion strength and relatively low surface area limited their applications [44, 45].

Among the photocatalytic reactors, the solar photoreactor with large illuminated surface area and efficient light utilization/distribution over the catalyst surface are considerably effective for photocatalytic CO_2 reduction applications. Basically, the solar photo-reactors are the most frequently utilized and involve three phase system where the catalyst bed is in a fluidized form and agitated to increase mass transfer between catalyst and reactants, thus providing high surface area to be illuminated [46]. In addition, higher light distribution and harvesting over the catalyst surface would also be possible utilizing reflector. Therefore, solar photoreactor with reflector could make higher CO_2 reduction to solar fuels with higher selectivity.

1.3 Problem Statement and Research Hypothesis

Conversion of CO_2 to solar fuels provides alternative ways for monitoring global warming and energy crises. The main challenges ahead in this field are described as below:

(a) Thermal conversion of CO_2 to solar fuels is a two-step process which required higher input energy. Therefore, the single step CO_2 reduction to hydrocarbon

fuels is possible through photo-technology process. Photoreduction of CO_2 with H_2O would be possible at normal temperature and pressure using solar energy.

(b) Although, photoreduction of CO_2 to fuels through photocatalytic reductions have several advantages, yet photocatalysts under investigations are inefficient to produce solar fuels with sufficient yield rates and selectivity. Among semiconductor materials, g-C_3N_4 is widely investigated because of abundantly availability, comparatively cheap and numerous other advantageous. However, it has lower light absorption efficiency, trivial photoactivity and selectivity for photocatalytic CO_2 reduction to solar fuels. Thus, photocatalytic efficiency of g-C_3N_4 can further be improved by combining with other semiconductor materials.

(c) Novel semiconductor ZnV_2O_6 would be the best candidate to be combined with g-C_3N_4 because of sufficient E_{CB} and E_{VB} potential for the conversion of CO_2 to fuels. ZnV_2O_6 has been investigated intensively owing to their unique physical and chemical properties including efficiently utilize the visible region of the solar spectrum owing to narrow band gap. However, it has never been reported for photoreduction of CO_2 to solar fuels under visible light irradiation. Besides, introduction of RGO onto the both semiconductors will provide Z-scheme photocatalytic system that can promote the photocatalytic conversion of CO_2 to fuel production to the ultimate point.

(d) Existing photoreactors have lower quantum efficiency because of inefficient harvesting and distribution of light irradiation over the catalyst surface. In addition, such types of reactors have lower exposed surface area, lower catalyst loading, and ineffective adsorption-desorption process and less mass transfer over the catalyst surface, resulting in lower yield rate and selectivity. Therefore, solar photoreactor will be productive to provide higher illuminated active surface area, higher adsorption-desorption and efficient mass transfer toward catalyst surface. Higher light distribution and harvesting over the catalyst surface would also be possible utilizing reflector, ultimately stimulating higher quantum efficiency toward efficient CO_2 reduction to selective solar fuels.

1.4 Research Objectives

The aim of this research is to design a solar photoreactor with reflector having cooling system and capable of enhancing CO_2 reduction and yield rates. Next novel nanocatalysts and process operating parameters are deliberated to maximize CO_2 reduction efficiency. The specific objectives of the research are:

(a) To synthesize and characterize Z-scheme rGO and g-C_3N_4 based ZnV_2O_6 nanocatalysts for solar energy applications;
(b) To test the performance of nanocatalysts for selective CO_2 photoreduction to solar fuels;
(c) To investigate and compare the performance of photoreactors for selective photocatalytic CO_2 conversion to solar fuels under UV and visible light irradiations;
(d) To determine kinetic and reaction rate parameters for understanding the role of nanocatalysts toward optimization of CO_2 reduction process.

1.5 Scope of Study

The scopes of this study are focused on resolving some of the fundamental problems related to lower CO_2 reduction efficiency and selectivity. In this perspective, synthesis and characterization of various nanocatalysts, reaction mechanisms of CO_2 reduction, oxidative-reductive model development and quantum efficiency analysis have been deliberated. Furthermore, the design of photoreactor is limited to the fabricating of solar photoreactor with reflector to maximize yield rates and products selectivity. The CO_2 reduction efficiency is related to maximize yield rates of desired products. Therefore, the specific research scope of this study is as follows:

(a) Novel ZnV_2O_6 nanosheets, ZnV_2O_6/g-C_3N_4 nanosheets, RGO combined ZnV_2O_6 nanosheets and Z-scheme ZnV_2O_6/RGO/g-C_3N_4 nanosheets photocatalysts are synthesized using one-step solvothermal method to

investigate the route of CO_2 photo-reduction to solar fuels. Nanocatalysts characterization are conducted using XRD, BET, FESEM, EDX, HRTEM, XPS, UV-Visible, RAMAN and PL spectroscopy in order to investigate the phase and crystal structure, surface morphology and mesoporosity, surface area and pore size distribution, metals transitions states and optical properties of catalysts.

(b) The role of nanocatalysts for photocatalytic reduction of CO_2 to solar fuels was firstly explored using solar photoreactor in which catalyst was distributed in the slurry aqueous system. The light source used was a 35W HID Xe lamp with a light intensity of 20 $mWcm^{-2}$ operated using high voltage power supply. The reducing agent employed was H_2O for CO_2 photo-reduction.

(c) In solar photoreactor design, a reflector was used to reflect the light to provide higher light irradiations to get higher reduction and yield rates. The photocatalytic reduction of CO_2 to solar fuels was investigated using H_2O as reducing agents. The performance comparison between fixed-bed (gas phase), solar photoreactor (liquid phase) and solar photoreactor with reflector (liquid phase) was conducted to investigate the efficiency of solar photoreactor with reflector.

(d) The catalysts were then used to photo-reduce CO_2 to obtain solar fuels using both UV and Visible light and their performances were compared based on the yield of fuels. The reaction mechanism and kinetic model were developed to find out the key parameters in CO_2 reduction applications.

1.6 Significance of Study

In this study, CO_2 was efficiency converted to CH_3OH, CO, CH_4 and H_2 in the presence of reducing agents and photocatalytic systems, thus confirming sustainable fuel productions. The solar photoreactor with reflector performance was very encouraging while the efficiency found was much higher than ever reported in the literature. However, several outcomes of this research are described below:

(a) New solar photoreactor with reflector system to investigate efficient CO_2 reduction to solar fuels.

(b) Novel ZnV_2O_6 nanosheets for stable and high-performance photo-induced CO_2 reduction to solar fuels.

(c) Novel indirect Z-scheme assembly of ZnV_2O_6/RGO/g-C_3N_4 nanosheets toward visible-light enhanced CO_2 reduction.

(d) New development in reaction rate and kinetic models.

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

1.7 Outline of Thesis

This thesis is divided into five chapters excluding all introductory pages, table of content and abstract. Chapter 1 presents the introduction, problem statement and research hypothesis, objectives, research scope, significance of study and outline of thesis. The literature survey, basics of photocatalysis and CO_2 photoreduction, previous works in photoreduction of CO_2, the photoreactor setups, characterization techniques, description of photocatalytic reactors and development of kinetic models were discussed in Chapter 2. Chapter 3 gives a detailed representation of the research methodology and order of the research, details of the methods used to synthesize the catalysts and carry out the photoreduction process. The results obtained from the experiments and analysis of characterization are discussed in Chapter 4. Chapter 5 concludes the thesis with inferences drawn and recommendations for further research.

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