DEVELOPMENT OF PHOTOCATALYST FOR CO_2 CONVERSION TO HYDROCARBON FUEL

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DEVELOPMENT OF PHOTOCATALYST FOR CO_2 CONVERSION TO HYDROCARBON FUEL

NURUL IZAAZ BINTI AZMI

Thesis submitted in fulfilment of the requirements
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STATEMENT OF AWARD FOR DEGREE

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of degree of Bachelor of Engineering Technology in Energy and Environment.

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ABSTRACT

Owing to the limited amount of energy sources and the recent effects of fossil fuel use on the global environment, the paradigm of energy supply is changing from one based on the use of carbon-rich rocks, peat, and liquid found in the Earth to one based on renewable sources, such as energy crops, sunlight, and wind. Several methods for reducing the carbon dioxide concentration in the atmosphere and preventing CO_2 emissions due to human activity have been investigated, such as investigating the sorption of CO_2 into new/functionalized materials; increasing the quantity of green carbon sinks (plants, phytoplankton, and algae containing chloroplasts); increasing the level of dissolved carbonate and its salts in sea water; or capturing CO_2 and transferring it to the bottom of the sea in a supercritical state.

Photocatalytic reduction of CO_2 to fuels using solar energy is an attractive option for simultaneously capturing this major greenhouse gas and solving the shortage of sustainable energy. To conquer the problem of increasing CO_2 in the atmosphere, a solution using TiO_2 to convert CO_2 into usable fuel are conducted. Basically, the approach centres on the concept of the large-scale re-use of CO_2 released by human activity to produce synthetic fuels, and how this challenging approach could assume an important role in tackling the issue of global CO2 emissions. There are three main objectives of this research which are to design, synthesis and develop an efficient modified nano-based TiO_2 to enhance the reduction of CO_2 to fuel, methane (CH_4) through photocatalyst, to study the material chemistry of modified Nano-based TiO_2 who enhance the process of the photocatalyst and to utilize the prepared photocatalyst for CO_2 conversion to CH_4 in term to reduce greenhouse effect.

The photocatalytic experiment conducted by synthesising TiO_2. Addition or doping with noble metal, such as platinum (Pt), palladium (Pd), silver (Ag) and gold (Au) ions allow extending the light absorption of band gap semiconductors to the visible light. Noble metals could be introduced to the surface of TiO_2 by various methods such as: electrolysis, chemical reduction, UV photoreduction, γ-reduction deposition from colloids or adsorption of metal clusters. The characterizations are

focused on optical and physical characterization. Then, the evaluation of photocatalyst process is carry out in a solid gas phase photoreactor. A tungsten – halogen lamp with high pass UV light filter are use as the visible light source. The CO_2 are bubbled through the water vapour into the chamber. The result is collected and analyse for the CH4 yield using gas chromatography system.

The information gained from this analysis will help to contribute towards a better understanding of the main parameters that affect the activity of photocatalysts and will ultimately lead to the optimized synthesis of more efficient photocatalytic material for the photocatalytic reduction of CO_2 to hydrocarbon fuels.

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CHAPTER 1

INTRODUCTION

1.1 General Information

Nowadays, the global warming issue getting crucial. This issue happened due to the atmospheric carbon dioxide (CO_2) growth rapidly from human being. Greenhouse gases are the main factor which causes the global warming. In the greenhouse gases, there is 72% of totally emitted CO_2, 18% of methane (CH_4) and 10 % of nitrous oxide (NO_X). CO_2 are the most important cause of global warming. CO_2 is inescapably created by burning fuels like e.g. natural gas, dieses, organic diesel, petrol and oil. International Panel on Climate Change (IPCC) predicted that atmospheric CO_2 level could reach up to 590 ppm by 2100 and the global mean temperature would rise by 1.9 °C (Li, An, Park, Majeda & Tang, 2014). The greenhouse gases will seriously impact in many different aspects, such as ice melting at the Earth's pole, fast rising sea level and increasing precipitation across the globe. CO_2 molecule is very stable which is not easily transformed into others chemical in a reaction. By using a photocatalyst, CO_2 can be served as a building block for the synthesis of other useful chemicals and chemical intermediates.

The photocatalyst for the conversion of carbon dioxide (CO_2) into hydrocarbon fuels with the visible light energy is a promising and eco-friendly approach to prevent the increase in greenhouse gases and exhaustion of fossil resources. Among the semiconductor materials like Titanium dioxide (TiO_2), Zinc oxide (ZnO), Tungsten oxide (WO_3) and Zinc Sulphide (ZnS), TiO_2 is one of the most promising photocatalyst due to its versatile characteristics including non-toxicity, low cost, high photocatalytic and chemical biologically inert. From the TiO_2 materials, TiO_2 nanoparticles are great interest in photocatalytic properties, hence it is used in antiseptic and antibacterial compositions. Furthermore, it is also been used in many application such as degrading organic contaminants and germs, UV-resistant material, manufacture of printing ink, self-cleaning ceramics and glass, coating. Nevertheless, TiO_2 nanoparticles also used in making of cosmetic products such as sunscreen creams, whitening creams, morning and night creams, skin milks and in the paper industry for improving the opacity of paper.

However, the photocatalytic activity of TiO_2 is limited by its low capability of absorption in the visible light and fast recombination rate of the photogenerated electron-hole pairs. The wide band gap (3.2 eV for anatase and 3.0 eV for rutile) of TiO_2 only can excited in UV range of spectrum ($\lambda < 380nm$). It covers only ~ 5% of the whole solar spectrum compare to the visible light spectrum (Sim, Leong, Phichiah & Shliza, 2015). Various studies have been carry out to improve the photocatalytic activity of TiO_2 by doping with noble-metals and non-metals. Besides, TiO_2 can be coupled with semiconductors. The noble metal such as gold (Au), silver (Ag), and copper (Cu), possess a great ability of visible light absorption due to existence of localized surface plasmon resonance (LSPR). LSPR is an optical phenomena which generated by light when it contact with conductive nanoparticles (NPs) that smaller than incident wavelength. As in surface plasmon resonance, the electric field of incident light can be deposited to collectively excite electrons of a conduction band, with the result being coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, dielectric environment and separation distance of NPs (Eleonora petryayeva, Ulrich J.krull, 2011). Moreover, noble metal will transfer the electron to TiO_2 and traps the electron in the metal TiO_2 nanostructures to minimize the surface charge recombination in TiO_2.

Further studies have been devoted to improve the optical absorption and increase the charge carrier transport Reduced graphene oxide (RGO) was used in the hybrids thus diminish the bandgap and minimize the electron-hole recombination rate. Graphene is a two-dimensional sp^2-hybrized carbon nanosheet which consist rich characteristic including high specific surface area, high electron mobility and tunable band gap. Liang et al. prove that the less deficient graphene-TiO_2 nanocomposite thin film resulted in larger improvement of photocatalytic for the photoreduction of CO_2 to CH_4. Tan et al. described that graphene-TiO_2 nanocomposite adopt the ultraviolet light (UV) produce a maximum CH_4 product yield of 0.135μmol g cat^{-1} h^{-1}, which is 2.1 and 5.6 fold higher than graphite oxide and pure anatase. These studies have shown that the enhancing effects of graphene on the photocatalytic of TiO_2 in hybrid materials.

Recent years, research shows that the graphene-TiO_2 nanocomposite is limited to photodegradation of organic pollutants. This encourages people to do more research toward the photocatalytic conversion of CO_2 to CH_4 with the assist of RGO as the proficient electron trapper to overwhelm the recombination of photoinduced electron-hole pairs.

1.2 Problem Statement

Nowadays, the issue of the CO_2 cause the global warming getting serious. CO_2 are the highest gases which contains around 72% of the greenhouse gases. This mean that CO_2 are the most important cause of global warming compare to another two gases (18% of CH_4 and 9% of NOx). CO_2 is inescapably created by burning fuels like e.g. natural gas, diesel, organic- diesels, petrol and oil. The emission of CO_2 have been increase dramatically within the last 50 years and still increase by almost 30% each year. The CO_2 is released to the atmosphere where it remain for 100 to 200 years. This lead the concentration of CO_2 in atmosphere increase, hence the earth temperature increase. The CO_2 gives the serious impact in different aspect such as ice melting at the Earth's pole, fast rising sea level and increasing precipitation across the globe (Li, An, Park, majeda & Tang, 2014).

Most of the photochemistry and photoelectrochemistry process involves the excitation of TiO_2 by photon with light energy greater than energy gap. However, the wide band gap (3.2 eV for anatase and 3.0 eV for rutile) only can excited with UV light which covers ~ 5% of the irradiation ($\lambda < 380$ nm) from the total solar spectrum. The solar spectrum consists of ~ 43% of the visible light and the remaining ~52% is infrared light. The availability of UV spectrum is marginal in comparison to the visible light spectrum. Hence it causes a major limitation of utilizing the UV source for its natural activation. Thus the present available TiO_2 is not suitable for the utilization of visible spectrum of solar energy. Therefore, the employment of solar energy for a photocatalytic process can be improved by altering the energy gap response of TiO_2 to the visible light region (Yu, Zhang, Cheng, & Su, 2007).

1.3 Objective

i. To synthesize highly pristine anatase TiO_2 nanoparticles (NPs) as template through a simple, facile and easy method.
ii. To identify noble metals from the periodic table along with a novel, smart, ease and sustainable method to incorporate them onto TiO_2 template for activating LSPR phenomenon.
iii. To investigate the contribution of carbon materials for visibility, electron mobilizing and charge carriers' transportation by wrapping it onto the synthesized composite photocatalysts.
iv. To characterize the prepared nanocomposite photocatalysts for its various intrinsic natures through crystalline phase analysis, morphology, elemental composition and optical properties.
v. To evaluate the visible light photocatalysis ability of the synthesized nanocomposite photocatalysts by converting CO_2 to CH_4.

1.4 Significant Of Research

Modified nano-based TiO_2 has great contribution towards the environment. In treatment of waste water, TiO_2 nanoparticles have the great potential for removal of organic pollutant from the waste water. However, it is not very practical in the industry because of its low oxidation rate. By comparing TiO_2 nanoparticle conversion process with other wastewater treatment such as activated sludge reactor, membrane bioreactor and etc., TiO_2 nanoparticle conversion no need to undergo the treatment for the sludge of the wastewater for secondary and tertiary treatment.

To solve the CO_2 problem permanently, it requires transformation of CO_2 into another useful or non-toxic compound. In our research, we use the principle of photoconversion to conquer the problem of increasing CO_2 in the atmosphere. The solution by using TiO_2 to convert CO_2 into usable fuel is conducted. The TiO_2 photoreduction's end product does not produce any toxic gases. The final gas produce is the dominant hydrocarbon, CH_4. The production of CH_4 will be another alternative to replace the fossil fuel in the future. Thus, by upgrading CO_2 to reusable hydrocarbon resources definitely would benefit humans and the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Background on Photocatalysis

2.1.1 Introduction

TiO_2 has been widely recognized as an excellent photocatalyst. It is known to have superb pigmentary properties, high adsorption in the ultraviolet region, and high stability which allows it to be used in various applications such as electroceramics, glass, and photocatalytic purification of chemical in air and water (Cheng Chee Kaan et al., 2012). The acceleration of a chemical transformation by the presence of a catalyst with light is called photocatalysis. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction and itself remaining unaltered at the end of each catalytic cycle (Haque et al., 2012). There are many semiconductor materials can be used as a photocatalyst. Semiconductors like TiO_2, ZnO, Fe_2O_3, CdS, ZnS etc. are all suitable materials to initiate a photocatalytic process (Kaan et al., 2012).

Photocatalysis, which initiates the breakdown of organic molecules into simpler aliphatic molecules and eventually to CO_2. An additional mineral acids are involved in several of the natural purification of aqueous system lagoons, ponds, streams, rivers and lakes. The process is well supported by the sunlight, a natural sensitizer. In 1976, the employment of ‘colloidal semiconductors’ and the beginning of catalysts to promote specific redox processes on semiconductor surfaces were developed (Kalyanasundaram, 1983). Since then, naturally occurring semiconductors that could boost this solar driven purification process have been proven in laboratory scale (Matthews, 1993). Wrapping up, the solar photocatalytic process can also be applied to removal of trace metals, destruction of organics, removal of inorganic compounds, degradation of natural organic matter and medical applications (Alex Omo Ibhadon and Paul Fitzpatrick, 2013).

2.1.2 Principle of Photocatalysis

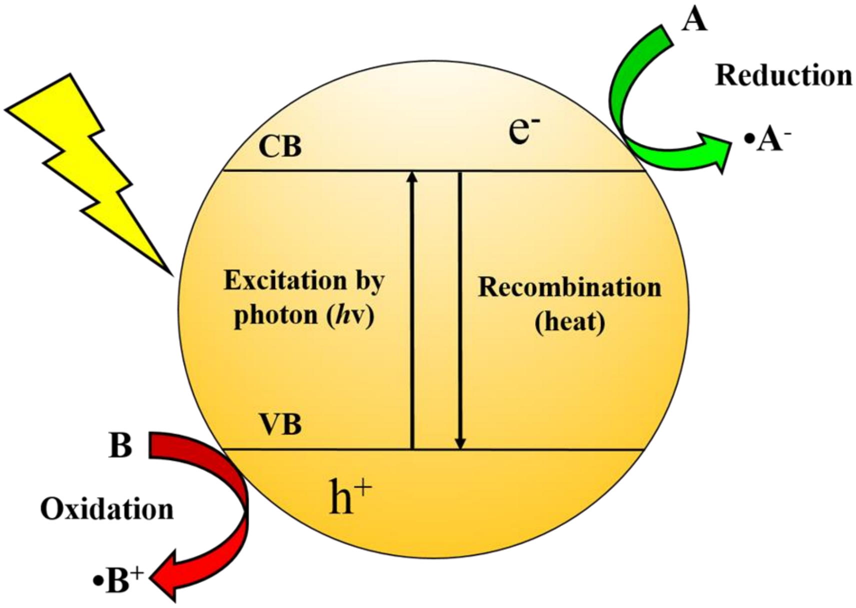

Figure 2.1 : Principle of Photocatalysis

Photocatalysis can be defined as the acceleration of a chemical reaction by either direct irradiation or by the irradiation of a catalyst that in turn lowers the activation energy for the primary reaction to occur. Photocatalytic oxidation (PCO), also known as heterogeneous photocatalysis, has been used since the mid-1970s to decontaminate water from harmful microorganisms and throughout the past decade has been applied to compensate for insufficiencies in spore destruction and decontamination in ultraviolet germicidal irradiation (UVGI) air disinfection systems (Hoffmann et al., 1995). Inertness to chemical environment and long-term photostability has made TiO_2 an important material in many practical applications, and, in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which TiO_2 is used as a desiccant, brightener, or reactive mediator (Alex Omo Ibhadon and Paul Fitzpatrick, 2013).

Photocatalysis processes involve the initial absorption of photons by a molecule or the substrate to produce highly reactive electronically excited states (Amy L. et al., 1995). When a photocatalyst is irradiated with photons with energies greater than that of the semiconductor’s band gap, Eg (eV), an electron is transferred to the CB, leaving behind a positive hole in the VB. The pair of photo excited charges that occurs within a particle is called an electron-hole pair (Alex Omo Ibhadon and Paul Fitzpatrick, 2013). The efficiency of the photocatalytic process is measured as a quantum yield which is defined as the number of events occurring per photon absorbed. The ability to measure the actual absorbed light is very difficult in heterogeneous systems due to scattering of light by the semiconductor surface. It is usually assumed that all the light is absorbed and the efficiency is quoted as an apparent quantum yield. If several products are formed from the photocatalytic reaction the efficiency is sometimes measured as the yield of a particular product (Amy L. et al., 1995).

The most common approach to categorize the trapping sites of electrons below the CB is purely based on their energy position in respect to CB and depicted as preexisting defect states,5,8–10 suggestively called ‘shallow’ and ‘deep’ traps. The deep traps are consensually associated to O_2 defect sites, namely vacancies, which are more abundant on TiO_2 surface due to unsaturated coordination related to crystal termination. The shallow traps on the other hand are a matter of intense discussion and there is not to date an unambiguous structural feature associated with them that is consensual (Fabio G. Santomauro et al., 2015).

The resistance between charge-carrier recombination and charge transfer is the one that determine overall quantum efficiency for interfacial charge-carrier transfer (Hoffmann et al., 1995). The band positions or flat band potentials of the semiconductor material is also of great importance which indicates the thermodynamic limitations for the photoreactions that can take place.

2.2 Graphene oxide

Graphene, which consists of a single atomic layer of sp2 two-dimensional (2D) hybridized carbon atoms arranged in a honeycomb structure, is a basic building block for all graphitic forms. The initial application of graphene was in the field of electronic devices, concentrated upon its electronic properties. As the research on graphene developed rapidly, it was soon realized that graphene possesses other exciting properties, such as high stiffness and strength, excellent thermal properties and promising biocompatibility (Jianchang Li et al., 2014).

The techniques developed for synthesizing graphene can be grouped into six major methods, i.e., mechanical cleavage, epitaxial growth, chemical vapor deposition (CVD), total organic synthesis, and chemical method. Recently, GO has gained more attention because it is functionalized easily with fluorescent probe and other compatible biomolecules (Liu, et al., 2010; Pham, et al., 2011). These unique properties of GO make it a promising nanomaterial for bioapplication. Industrially produced GO could be used for wide range of application such as solar cell (Xinjuam, et al., 2012), hydrogen storage(Wang, et al., 2007), transparent conductive films (Park, et al., 2010), Polymer composite (Zhang, et al., 2009, Eda and Chhowalla, 2009), Paper like materials (Dikin, et al., 2007), biomedicine (Mohanty and Berry, 2008; Yousefim, et al., 2012; Bykkam, et al., 2013), fabricating nanoelectronic devices (Bunch, et al., 2007), energy storage devices (Liu, et al., 2010), biosensors (Prabhakar, et al., 2008; Lu, et al., 2009; Zhou, et al., 2010; Yancai, et al., 2013), catalysis (Chauhan, et al., 2011) and transparent electrodes (Zhang, et al., 2010).

GO also possesses nontoxological effects and hence can be widely used in medicinal research. Due to antimicrobial activity of GO, they can also be employed in dental resin composites, bone cement, ion exchange fibers and coatings for medical devices, biosensors and nano-biotechnology research. The results showed that GO nanoparticles presented good antibacterial activity effective against common human pathogenic microorganism (Bao, Qi, Dun Zhang and Peng Qi, 2011).

The combination of graphene with TiO_2 can create composites with both the outstanding characters and functions of two components and lead to some additional novel properties. Thus, graphene-based photocatalyst possesses numerous opportunities for the photocatalytic CO_2 reduction field. Due to the unique structure and excellent electronic, thermal and mechanical properties, graphene is expected to be catalyst supports. The combination of graphene with TiO_2 can create composites with both the outstanding characters and functions of two components and lead to some additional novel properties. Thus, graphene-based photocatalyst possesses numerous opportunities for the photocatalytic CO_2 reduction field (Liu, Jinghua, et al., 2016).

2.3 Noble Metal

Metal nanoparticles are widely used to construct structures that possess unique electric, photonic and catalytic properties such LSPR, SERS and SEF (Zhang, YuJuan, et al., 2012). Nanoparticles of Ag, Au, Cu, Fe and its oxides, Pd and Pt have found applications in catalyzing reactions, which offer immense scope for green chemistry. Fe and its oxide nanoparticles are excellent materials for environmental remediation. Nanoscale materials are used as sorbents for contaminants, in nanofiltration and in reactive membranes. The use of metal nanoparticles in sensing could bring about a revolution in biology, healthcare, military and day-to-day life (Nair, A. Sreekumaran, et al., 2007).

In particular, the extinction spectra of noble metal nanoparticles are dominated by LSPR. These resonances are attributed to a coherent excitation of the CB electrons, excited by means of an electromagnetic field. In the presence of the oscillating electromagnetic field of the light, the free electrons of the metal nanoparticle undergo a collective coherent oscillation with respect to the positive metallic lattice (Hu, Chun, Tang, Yuchao, Jiang, Zheng, Hao, Zhengping, Tang, Hongxiao and Wong, Po Keung, 2003).

Addition or doping with noble metal, such as Pt, Pd, Ag and Au ions allow to extend the light absorption of band gap semiconductors to the visible light. Noble metals could be introduced to the surface of TiO_2 by various methods such as: electrolysis, chemical reduction, UV photoreduction, γ-reduction deposition from colloids or adsorption of metal clusters. It was proved that doping with $[Pt_3(CO)_6]$n2- (n=3-10) clusters could enhance the photoconversion yield by inhibition of the electron hole recombination (Grabowska, Ewelina, Hynd Remita, and Adriana Zaleska, 2010).

The effect of the metal modification on the photocatalytic activity depends on the type of metal, metal precursor concentration used during synthesis and the origin of titania. Generally, the surface modified with Ag, Au and Pt clusters exhibits better efficiency in phenol photooxidation than TiO_2-based photocatalysts. It was found that titania surface modification with Ag and Pt enables the increase of the photocatalytic activity both under UV and visible light irradiation (Grabowska, Ewelina, Hynd Remita, and Adriana Zaleska, 2010).

2.4 CO_2 reduction

The past few decades have witnessed the problem of global warming, which is dominantly caused by CO_2 emissions from fossil fuel consumption. Therefore, seeking for any alternative to minimize CO_2 emission has attracted increasing attention all over the world. The traditional method used to solve this problem is carbon capture and storage, but in fact this problem has never been solved radically because CO_2 does not convert into other substances. The photocatalytic reduction of CO_2 into hydrocarbon fuels was found to be a prospective way (Liu, Jinghua, et al., 2016). The energy grade of CO_2 is low from a thermodynamic perspective, accounting for why any transformation to hydrocarbon requires energy infusion. The energy source should be provided without producing more CO_2, such as solar energy (Wu, Jeffrey, and Hung-Ming Lin, 2005).

Photocatalytic CO_2 conversion is a complicated combination of photophysical and photochemical processes. The redox reaction is initiated by photoexcitation when the energy of photons equal to or greater than the band gap of a semiconductor is received by the photocatalyst. Then the electrons are excited from the VB to the CB (Li, Kimfung, et al., 2014).

CHAPTER 3

METHODOLOGY

3.1 Material

Titanium (IV) chloride ($TiCl_4$, 99.9%), graphite flakes (C, 99%), sliver nitrate ($AgNO_3$, 99.9%), tetrahydrofuran (THF, 99%), ethylene glycol (C_2H_6O, 99.8%), benzyl alcohol (C_7H_8O, 99.8%), potassium permanganate ($KMnO_4$, 99.9%), sulphuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), hydrogen chloride (HCl, 37%) denatured ethanol (99.7%) and deionized water.

3.2 Synthesis of TiO_2

Synthesis of TiO_2 is done by adding drop by drop of 1 ml of $TiCl_4$ in to 20ml of anhydrous benzyl alcohol while the solution is stirred. Observe the colour of the solution which will turn to red colour and then to orange colour and lastly will remain in yellowish colour with white precipitate at the bottom of the beaker. The stirring process will last for 24 hour and aged for 21 days at room temperature. Next, recover the white precipitate by centrifugation at 300rpm for 30 minutes and rinse it thoroughly with 20mL of ethanol and follow by 20ml of tetrahydrofuran (THF) for 2 times. This process is repeated for 3 times to ensure removal of Cl^- anions. Lastly, dry the TiO_2 sample at room temperature. (Leong et al., 2015).

3.3 Synthesis of Ag-TiO_2

0.2g of TiO2 is added into the mixture of ethylene glycol which contains AgNO3. The mixture is then stirred continuously for 15 minutes under visible light. After the stirring process, the white precipitate formed is separated by centrifugation at 2000 rpm for 5 minutes. The result is then retrieved and washed it with ethanol and distilled water. This process is repeated for 2 times and lastly dries it overnight at 90℃. (Leong et al., 2015)

3.4 Synthesis of RGO

According to Simplified Hummers method, graphene oxide was synthesized by adding 3.0g of natural graphite powder in the mixture of 400ml of H_2SO_4 and 18g of KMnO4. Then, stir the mixture for 3 days to complete the oxidation process. H_2O_2 solution is then added to stop the oxidation process. Next, graphite oxide is wash with 1 M of HCl and deionized water. During the washing process, the graphite oxide underwent exfoliation to form GO gel. After that, let the GO gel to dry in vacuum at 60°C for 24 hour to obtain graphene oxide solid (GO solid). (Hummers, W.S et al., 1958)

3.5 Synthesis of RGO-Ag/TiO_2

After getting the GO solid, dissolve 0.2g of GO solid in the deionized water under ultrasonic condition for an hour. Then add 1g of Ag/TiO_2 into the yellow brown solution (GO solution) and stir for 1 hour until homogenous phase appear. Next, the homogeneous solution is autoclaved at 180°C for 6 hour. This hydrothermal treatment reduce GO to RGO. After 6 hour, retrieve the result through centrifugation and wash it thoroughly through deionized water. Dry the RGO-Ag/TiO_2 suspension at room temperature. (Leong et al., 2015).

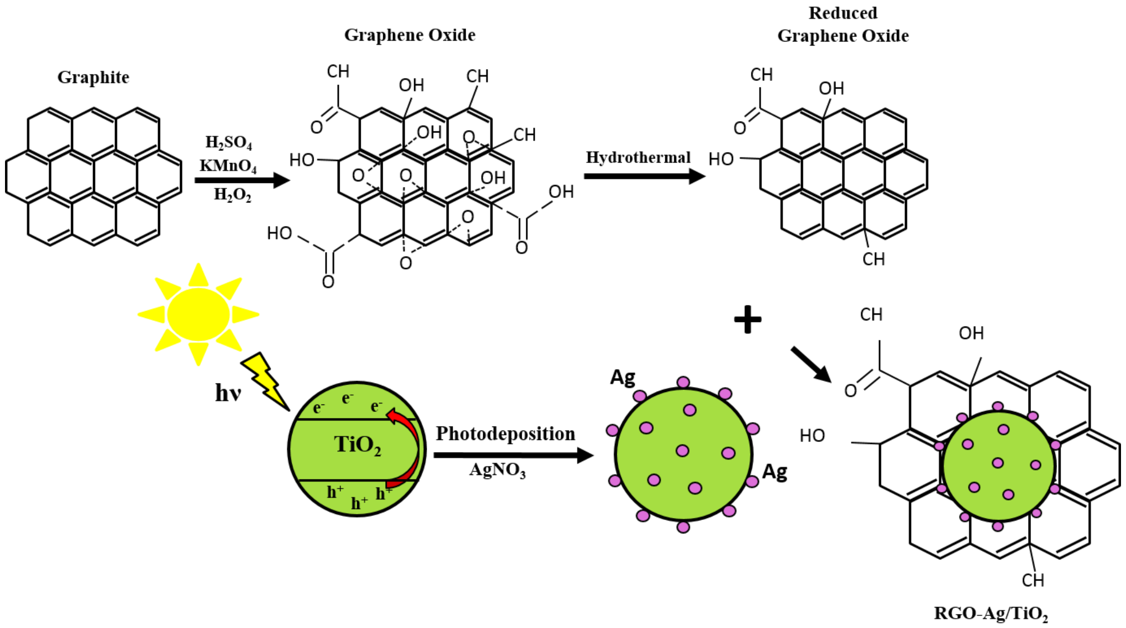

Figure 3.1: Methodology of synthesising RGO-Ag/TiO_2

3.6 Characterization

The x-ray diffraction (XRD) patterns of the prepared photocatalyst are studied with Burker AXS instrument using Cu Kα (λ = 1.5406 Å) radiation operating at 40 kV and 40 mA for the angle of diffraction 2θ between 10 and 80 degrees with an angular step of 0.05° s^{-1}. It is used to investigate the crystalline phase composition and the grain size of the photocatalyts. The physical structure of the sample are measured by field emission scanning electron microscope (FESEM) at an accelerating voltage of 20 kV (Hitachi SU-8000). The transmission electron microscopy (TEM) study is carrying out by Zeiss (EM 900 TEM, Zeiss, Germany). Energy dispersive x-ray spectroscopy (EDS) detector from EDAX Inc., and a post-column imaging filter (Quantum SE, Model 963) from Gatan Inc are used to observe the specific structural and determine the composition of the synthesis material. UV visible spectrophotometer is used to measure the ability of the prepared photocatalysts to absorb visible light.

Figure 3.2: FESEM machine used in UMP central lab.

Figure 3.3: XRD machine in UMP central lab

3.7 Photocatalytic Reduction of CO_2

The phtocatalytic reduction of CO_2 is carry out in a solid gas phase photo reactor. The experiment setup is shown as the schematic diagram in Figure 3.1. A 500 W tungsten – halogen lamp with high pass UV light filter are use as the visible light source. Synthesis powdered sample, RGO-Ag/TiO_2 with petri dish are place into the chamber together with a total volume of 9.8 mL highly purified CO_2 (99.9%) which are supply by the mixture of CO_2 and water vapour. The CO_2 are bubbled through the water vapour into the chamber. In order to eliminate the impurities, CO_2 gas was eject through the reactor at a flow rate of 300 mL min^{-1} for 1 hour and then maintain the flow rate at 100 mL min^{-1} for the whole experiment. The result is collected and analyse for the CH_4 yield using gas chromatography system (Sim et al., 2015).

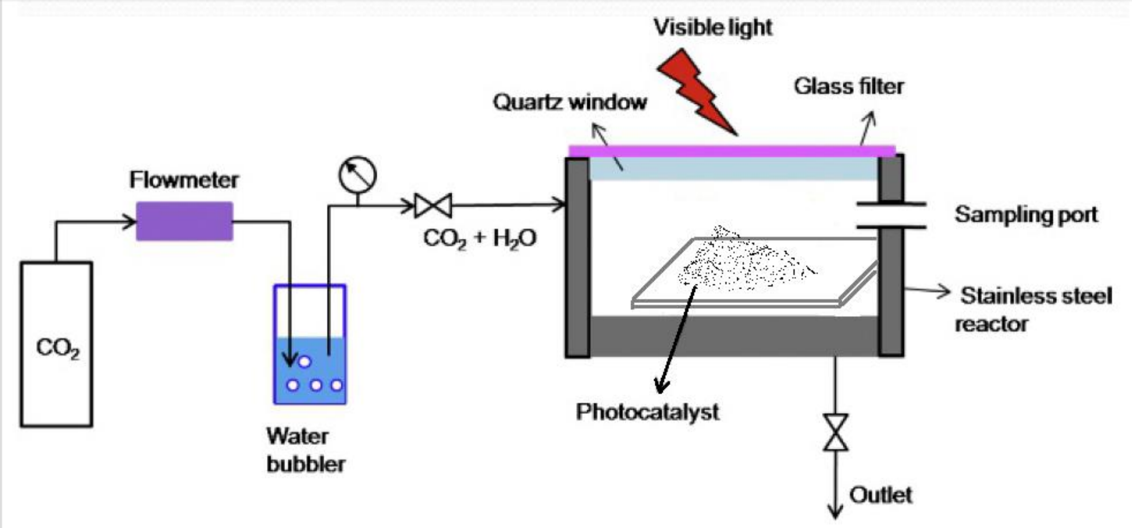

Figure 3.4: Schematic diagram of solid gas phase photoreactor

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 Characterization

The anatomy of the prepared photocatalysts is shown in Fig. 4.1. The top view FESEM image in Fig. 4.1 presents the uniformly stacked and vertically orientated nanotubular structure of pure TiO_2 with inner diameter ranging between 100and 120 nm and a wall thickness of 15 nm. Morphology of TiO_2 remains unchanged after the encapsulation of the impurities.

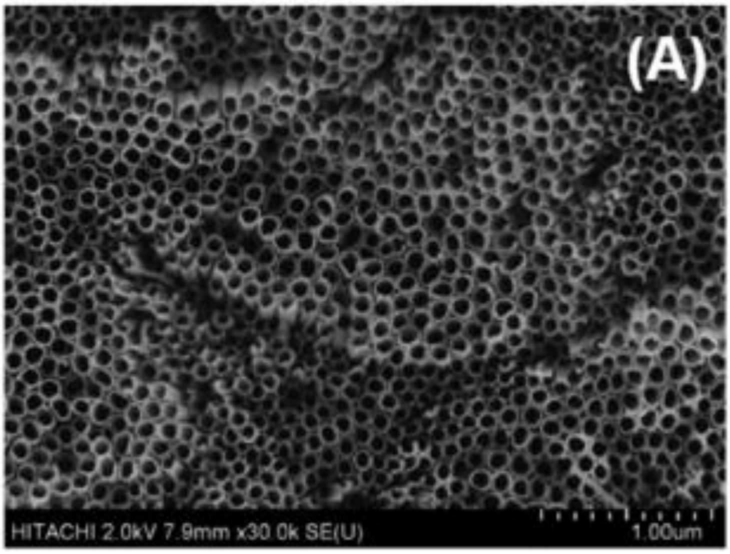

Figure 4.1: Top view of pure TiO_2

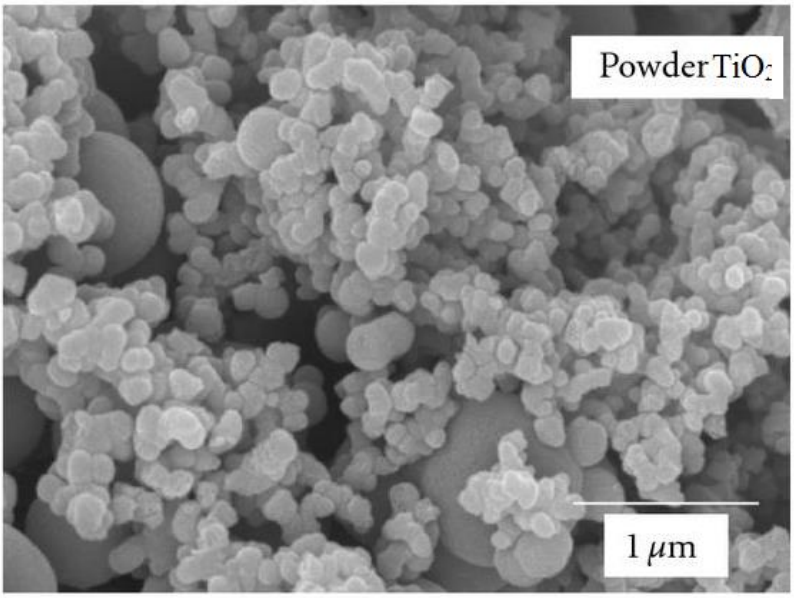

Figure 4.2: Powdered Tio_2

In analyzing the light absorption of the synthesized materials, UV-visible absorption spectroscopy analysis was executed and considerable red shift towards visible light region is clearly observed for RGO-TiO2 and RGO-Ag/TiO2 indicating narrow band gap energy with the introduction of RGO. This significant shift ascertains the incorporation of RGO in the composite through Ti—O—C bond. The existence of Ag NPs on the surface of TiO2 significantly oscillated the dielectric constant surrounding the matrix leading to the visible light absorption. It was found that after the incorporation of RGO, the band gap energy of TiO2 was tuned to 2.9 eV. The reduction in band gap was attributed to the formation of Ti—O—C bond, where the electrons on the surface of TiO2 are bonded with unpaired π-electrons and leading to a shift upwards the valence band edge. The observed phenomenon enhanced the RGO-Ag/TiO2 with a notable visible light performance.

Figure 4.3: UV-visible absorption spectrometer used in UMP central lab.

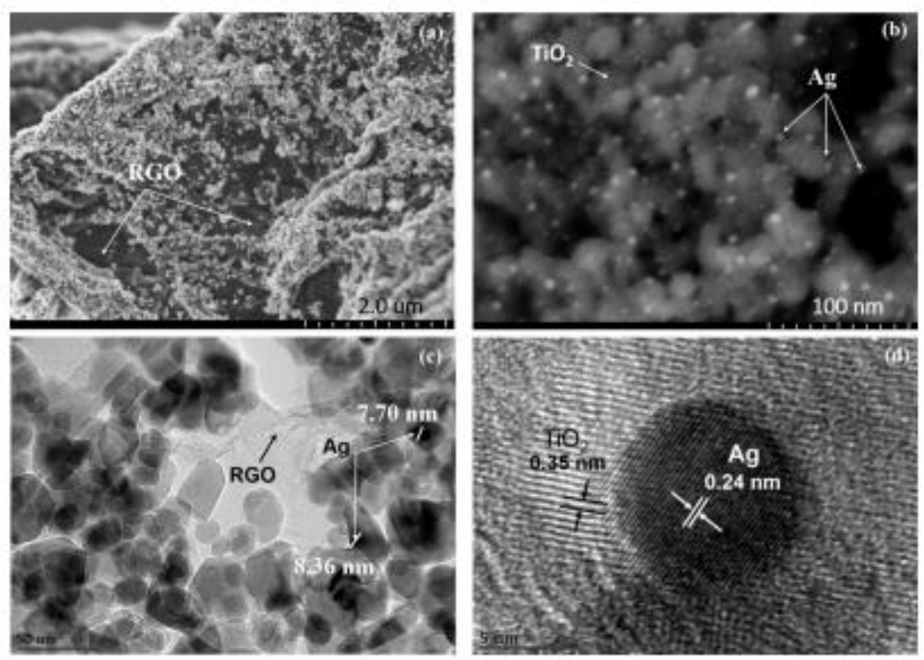

Figure 4.4: Physical surface structural of RGO-Ag/TiO_2 (a) and (b) TEM image of RGO-Ag/TiO_2. (c) and (d).

The photoluminescence spectra for the prepared photocatalysts are well proven from the spectrum that the deposition of RGO and Ag NPs drastically prolonged the lifetime of the charge carriers. This is owing to the trapping of the photo-excited electrons and high charge carrier mobility of RGO. A more active separation of electron-hole pairs was observed after incorporation of Ag NPs. This resulted from the effective electrons transfer from TiO_2—Ag NPs-RGO. Transient photocurrent responses were studied to provide additional evidence for the separation of the photoelectrons and holes of the prepared photocatalysts. The higher photocurrent possessed by RGO-Ag/TiO_2 as compared to rest demonstrated the higher efficiency of the charge separation in the composite. A more active separation pf electron-hole pairs was observed after incorporation of Ag.

When these NPs get intimated with RGO, it further transfers the electron to the surface of RGO. Hence, it further suppresses recombination and thereby increase the overall phpotocatalysis performance. Localized surface plasmon resonance (LSPR) phenomenon triggered by the noble metal alsp well contributed for the visible loght enhancement. Ag surface plasmon excited by the presence of visible light and collective electron oscillation generates high concentration of energetic electrons at its surface. Movement of electrons from Ag to RGO surface prolongs the life span of the charge carriers.

4.2 Photocatalytic reduction of CO_2

All the prepared photocatalyst were prepared for evaluation of conversion of CO_2 with water vapour to CH_4 under visible light irradiation. A few control experiments were conducted to confirm that the CH_4 yield was mainly contributed by the photocatalytic reduction of CO_2. The control experiments were conducted under the conditions of:

1. Without light irradiation with the presence of photocatalysr and the flow of CO_2/H_20,
2. Absence of photocatalyst under the flow of CO_2/H_20 and light irradiation,
3. Absence of vapor with the presence of photocatalyst, CO2 flow and light irradiation, and
4. Under N_2 and H_2O vapour flow in the presence of photocatalyst and light irradiation.

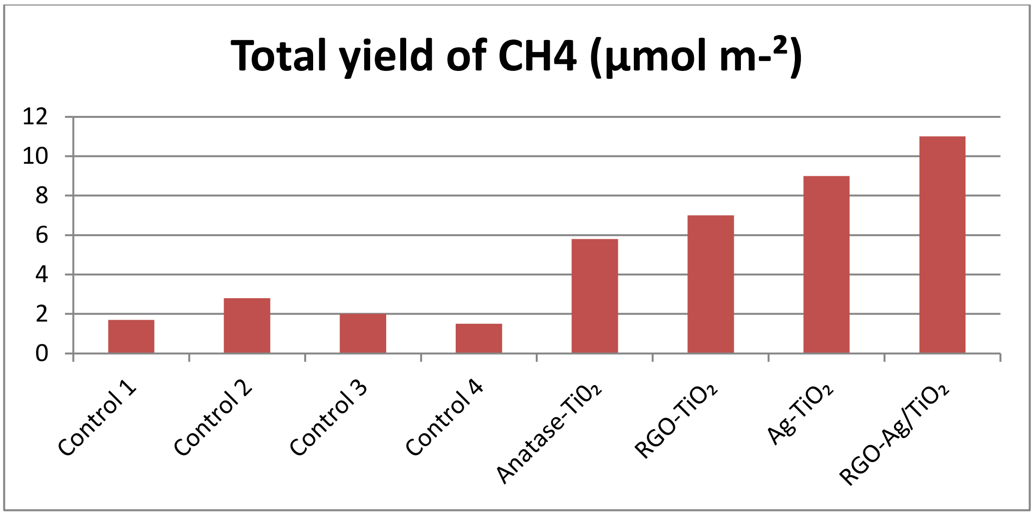

Figure 4.5: Total yield of CH_4

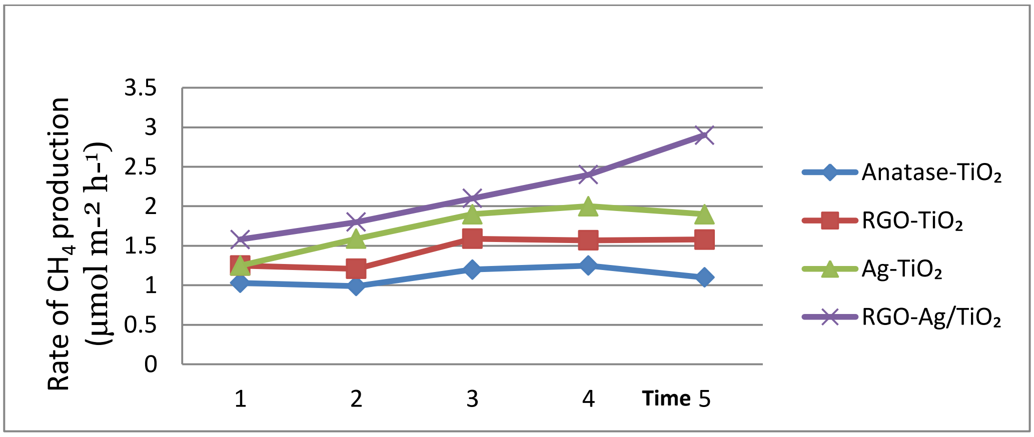

Figure 4.6: Rate of CH_4 production

From the control tests, the reduction of CO_2 occurred mainly in the presence of photocatalyst, reactants CO_2/H_20 and light irradiation. The total CH_4yield follows an ascending order of TiO_2 (5.67 µmol m–^{2}) < RGO- TiO2 (6.89 µmol m–^{2}) < Ag- TiO_2 (9.03 µmol m–^{2}) < RGO-Ag/ TiO_2 (10.96 µmol m–^{2}). As shown in Fig 4.4, TiO2 achieved minimal CH4production rate with a maxi-mum yield of 1.28 µmol m–^{2}h–^{1}. It is known that pure TiO_2 s are not responsive to visible light due to its large band gap.

CHAPTER 5

CONCLUSION

Global warming is very crucial problem that occurs nowadays. CO_2 emissions are one of the main causes of global warming. In our proposal, the synthesis of photocatalyst, RGO-Ag/TiO_2 provides an opportunity to tackle the causes of global warming. The combination of TiO2, RGO and Ag which can be use under visible light as a medium to convert the CO2 into hydrocarbon fuel $CH_{4.}$ In conclusion, visible light promoted composite TiO_2 was successfully achieved with the support of Ag and RGO. The accomplishment of synergised effect of RGO and Ag demonstrate and excellent photocatalysis under visible light irradiation. Thus, the present study exhibited significant contribution of the each element in the composites for the enhancement of titania towards utilising non-renewable energy sources for sustainable treatment.

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