PHOTOREDUCTION OF CARBON DIOXIDE TO METHANOL USING COPPER MODIFIED CARBON NITRIDE AND TITANIUM DIOXIDE NANOCOMPOSITES

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A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

JULY 2016

To my Wonderful Father, Mother and Siblings.

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to the Almighty God for blessing me with this topic.

Firstly, I would love to express my sincere gratitude to my supervisor Prof. Dr. Nor Aishah Saidina Amin for her continuous support throughout my research, for her patience, motivation, enthusiasm, wealth of knowledge and experience. Her 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 Dr. Muhammad Tahir for introducing me to this topic. For always being there any time I needed an advice or assistance, for the drive towards research and publication that you instilled in me. 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.

Words cannot express how grateful I am to my mother, father and siblings for all of the sacrifices that they made on my behalf. Your prayers for me was what sustained me thus far. I would also like to thank all my family members, especially my dear Aunty, Toyin Adegborioye and her husband for supporting me throughout my academic journey.

ABSTRACT

Photoreduction of CO_2 to useful chemicals have shown promising results from the research on CO_2 conversion and utilization. The objective of this study is to synthesize copper and carbon nitride based titanium dioxide nanocomposites for selective photoreduction of carbon dioxide to methanol under visible light irradiations. The nanocomposites were synthesized by a chemical precipitation method and characterized using XRD, FT-IR, FESEM, TEM, DRS, BET and XPS. The XRD results confirmed the presence of TiO_2, g-C_3N_4 and Cu in the nanocomposite by their characteristic peaks. The doping of Cu metal reduced the intensity of the PL emission and the rate of recombination. The most effective catalysts was g−C_3N_4/(3% Cu/TiO_2) which gave a maximum methanol yield of 948.14µmol/g.cat after 2 h. Cu doped TiO_2 enhanced its photoactivity by fostering carrier separation. The position of Cu in the composite affected the distribution of electrons and hence the photo-activity. Parameters investigated were weight percent ratio, effect of time and stability. The position of Cu in the composite affected the distribution of electrons and hence the photo-activity. After 8 h of photoreaction, a maximum CH_3OH yield of 2574 µmol/g. cat was obtained using visible light. The ratio of g-C_3N_4 to Cu/TiO_2 dictated the efficiency of the composite and the visible light was seen to demonstrate higher efficiency compared to the ultraviolet light. The higher emitting power UV light provided more photons for photoexcitation of more electrons, but photo-oxidation of CH_3OH to HCOOH affected the product yield while using UV light. The low band gap, electronic structure and light absorption capacity of g-C_3N_4 assisted in the transfer of photogenerated electrons to Cu/TiO_2 in the composite thereby aiding maximal usage of the irradiated light. Cu/TiO_2 demonstrated a high selectivity for photoreduction of CO_2 to CH_3OH in the nanocomposite. The photostability of the composite was maintained even after three cycles. Possible reaction mechanisms were proposed to understand the type of catalysts and light irradiations on yield and selectivity.

ABSTRAK

Tindak balas penurunan CO_2 oleh cahaya kepada bahan kimia berguna telah menunjukkan keberhasilan penyelidikan mengenai penukaran CO_2 dan penggunaannya. Objektif kajian ini adalah untuk mensintesis tembaga (Cu) dan karbon nitrat (g-C_3N_4) berasas nanokomposit titanium dioksida (TiO_2) untuk tindak balas penurunan terhadap CO_2 kepada methanol di bawah radiasi cahaya. Sintesis nanokomposit disintesis dijalankan melalui kaedah pemendakan dan dikelaskan/dicirikan menggunakan XRD, FT-IR, FESEM, TEM, DRS, BET and XPS. Hasil kajian XRD menunjukkan kewujudan TiO_2, g-C_3N_4 dan Cu di dalam nanokomposit berdasarkan ciri-ciri puncaknya. Penambahan bendasing seperti logam Cu telah mengurangkan keamatan pemancaran PL dan kadar penggabungan semula. Mangkin yang paling berkesan ialah g−C_3N_4/(3% Cu/TiO_2) dimana telah menghasilkan metanol secara maksimum 948.14µmol/g.cat selepas 2 j. Penambahan Cu ke atas TiO_2 melalui kaedah pemisahan pembawa telah meningkatkan tindak balas aktiviti penurunan cahaya. Tindak balas penurunan CO_2 kepada CH_3OH oleh cahaya didalam nanokomposit telah menunjukkan pemilihan tinggi untuk Cu/TiO_2. Kedudukan Cu didalam komposit memberi kesan ke atas pengagihan elektron-elektron dan tindak balas aktiviti penurunan cahaya. Parameter kajian ialah nisbah peratus berat, kesan masa dan kestabilan Selepas 8 j tindak balas penurunan cahaya, sebanyak 2574µmol/g CH_3OH terhasil dibawah radiasi cahaya. Nisbah g-C_3N_4 kepada Cu/TiO_2 telah menunjukkan kecekapan komposit dan cahaya nampak berbanding dengan cahaya ultraungu. UV yang dipancar akan merangsang penghasilan lebih banyak foton-foton untuk proses pengujaan elektron-elektron walaubagaimanpun, pengoksidaan CH_3OH kepada HCOOH akan menjejaskan penghasilan produk. Pemindahan elektron-elektron melalui cahaya kepada Cu/TiO_2 didalam komposit dibantu oleh jalur gelombang rendah, struktur elektronik, dan kadar penyerapan cahaya oleh g-C_3N_4 sekaligus mengawal penggunaan cahaya yang terang. Kestabilan foto didalam komposit dikekalkan selepas 3 kitaran. Kepelbagaian dalam tindak balas mangkin dan radiasi cahaya turut dicadangkan untuk menyatakan sebarang kemungkinan dari mekanisme dan hasil pemilihan tindak balas tersebut.

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LIST OF ABBREVIATIONS

BET - Brunauer Emmett Teller
CB - Conduction Band
CCR - Carbon Dioxide Capture and Recycle
CCS - Carbon Dioxide Capture and Storage
CFCs - Chlorofluorocarbons
CNT - Carbon Nanotube
DME - Dimethyl Ether
DMT - Dimethyl triphthalic Acid
DRS - Diffuse Reflectance Spectra
EDX - Energy Dispersive Electron Microscope
EPA - Environmental Protection Agency
FESEM - Field Emission Scanning Electron Microscope
FFV - Flexible Fuel Vehicles
FID - Flame Ionization Detector
FTIR - Fourier Transform Infrared Spectroscopy
GAW - Global Atmosphere Watch
GC - Gas Chromatography
GHG - Greenhouse gas
HOMO - High Occupied Molecular Orbital
HVH - Higher Heating Value
ICE - Internal Combustion Engine
JCPDS - Joint Committee on Powder Diffraction Standards
LHV - Lower Heating Value
LSPR - Localized Surface Plasma Resonance
MWCNT - Multiwall Carbon Nanotube
MTBE - Methyl tertiary butyl ether
NEXAFS - Near edge X-ray absorption fine structure

NW - Nanowire
PE - Polypropylene
PET - Polyethylene
PL - Photoluminescence
PVC - Poly Vinyl Chloride
TCC - Tag Closed Cup
TOC - Tag Open Cup
UV - Ultraviolet
UV-Vis - Ultraviolet-Visible
VB - Valence Band
VLR - Visible Light Responsive
TEM - Transmission Electron Microscopy
XANES - X-ray absorption near edge structure
XPS - X-ray Photoelectron Spectroscopy
XRD - X-Ray Diffraction
1D - One-Dimensional

LIST OF SYMBOLS

ρ - Rho
γ - Gamma
λ - Lambda
μ - Mu
α - Alpha
ϕ - phi
θ - Theta
δ - delta
Δ - Delta
φ - Varphi
β - Beta
σ - Sigma
π - Pi

CHAPTER 1

INTRODUCTION

1.1 Problem Background

Global warming is considered to be one of the major environmental concerns of mankind today (Tahir and Amin, 2013). One of the major hazards from industrialization and technological advancement is the unguarded release of carbon dioxide (CO_2). Combustion of fossil fuel is the main source of greenhouse gas emission, which ultimately leads to global warming. It is gradually destroying the earth's climate and making survival tougher than ever (Olah *et al.*, 2006).

CO_2 can be perceived to be a safe gas to some extent since it is exhaled by man and animals and absorbed by plants but if its percentage in the atmosphere is not checked it could become a potential threat to the ecosystem and its occupants. This has generated massive attentions as it is a problem that has ripple effects such as global warming which is the major challenge in the world at the moment. The environment is under a lot of stress and a sustainable immediate solution is essential (Ali *et al.*, 2015).

Several options exist for global warming resolution and they can be categorized into two alternatives: eliminating the sources of greenhouse gases and capture of the gases. The first option cannot totally be accomplished because the comfort of man, industrial development and advancement are tied to most of these sources (Jiang *et al.*, 2010). This leaves us with the option of reducing the concentration of CO_2 in the atmosphere by capturing the released CO_2 and providing other alternatives which are not CO_2 producing. One way of doing this is to capture the CO_2 and store it in oceans, depleted coal seams etc. This option is CO_2 capture and storage also known as Sequestration, but it is expensive therefore unsustainable. The alternative and preferred option is to convert the captured CO_2 into valuable bulk chemicals such as methanol etc. Technologies for capturing CO_2 from flue gas includes absorption & adsorption of gases, the use of permeable membranes, cryogenic distillation etc. Many of these methods are not economically feasible (Cheah *et al.*, 2016).

Although it is obvious that CO_2 is a major cause of global warming and other environmental mishaps, another issue of concern in the world today is energy and its conservation. As of today, the largest percentage of the world energy demand is met through the deployment of fossil fuels and if more alternatives are not focused on this might not change in decades to come. The worlds reserve of natural gas is approximately 1014 m^3 which is a large portion of the worlds energy in total. In comparison to crude oil reserve, natural gas storage will remain longer and is hence a better option. Nations who are major consumers of petroleum and petroleum products constantly face problems due to the use of fossil fuels, geological spread and political supremacy of key petroleum raw materials (Aruchamy *et al.*, 1982; Moritis, 2004). One other viable substitute for fossils is nuclear energy except it is non-renewable and is destructive. To this end, an alternative source of energy which provides a simpler and cleaner fuel is a better option. CO_2 conversion and utilization provides us this alternative – turning CO_2 into a raw material for useful chemicals.

1.2 Photocatalysis as a viable route for CO_2 Conversion and Utilization

The conversion and utilization of captured CO_2 is a better option compared to sequestration, as it is a win-win approach. CO_2 conversion techniques include: - electrochemical (Li *et al.*, 2016), photochemical (Grebenshchikov, 2016), thermo-chemical (Dufour, 2016), radio-chemical (Yadav and Purkait, 2016), biochemical (Cheah, *et al.*, 2016), photoreduction and photo-electrochemical reduction processes (Apaydin *et al.*, 2016; Prasad *et al.*, 2016). For certain reasons such as cost of electricity (electrochemical), low efficiency (photochemical), one of the best methods for CO_2 conversion is the photocatalytic method in which solar energy is transformed and stored as chemical energy. Photocatalytic reduction of CO_2 is a clean, low cost and environmentally safe process (Cybula *et al.*, 2012).

The photocatalytic process involves direct absorption of photons by the photocatalyst. These photons must have band gap energies equal or greater than that of the photocatalyst in order to generate electron hole pairs. This is the initial step followed by reactions which will take place as a result of the excitation and energy transfer of the electrons to the reactants adsorbed on the photocatalyst. Although photoreduction of CO_2 is a multi-step reaction which is thermodynamically uphill it remains a very feasible and promising process (Indrakanti *et al.*, 2009). Photocatalysts provide the most viable method for harvesting solar energy with their reversible oxidation-reduction capabilities. They reduce CO_2 to form hydrocarbons such as methane and ethanol and essentially take exhaust and turn it back to fuel (Graham *et al.*, 2012). Considering the numerous benefits that can be derived from photocatalytic conversion of CO_2 to useful chemicals, this study focuses on the photocatalytic reduction of CO_2 to CH_3OH.

The research on photoreduction of CO_2 to methanol is a progressive one, a number of researches have been conducted using various photocatalysts. In terms of photocatalysts, TiO_2 remains the most researched of all photocatalysts owing to its exceptional properties though it is limited by its large band gap (3.2 eV) (Tahir and Amin, 2013). This limitation-necessitated modification of TiO_2 and one of the common modification methods is doping with metals (Cu (Slamet *et al.*, 2009), Ag (Liu *et al.*, 2014), and Au (Neaţu *et al.*, 2014) etc.). One notable research on CO_2 photoreduction to CH_3OH is that of (Slamet, *et al.*, 2009) involving the use of Cu doped TiO_2. A very good yield of methanol was obtained using 3% Cu/TiO_2 to photoreduce CO_2. Other alternative methods for modification include - non-metal (N) doping (Tahir and Tahir, 2016), co-catalyst (Prasad, *et al.*, 2016), formation of heterostructures (Li *et al.*, 2015), use of nanocomposites (Gusain *et al.*, 2016) etc. The results obtained from the photocatalysts modified using these methods are better than that of pure TiO_2. Recently, the use of g-C_3N_4 as a photocatalyst have increased due to its unique properties. It is thermally and chemically stable, can be prepared easily from nitrogen containing precursors, it is non-toxic, possess a low band gap of approximately 2.7 eV and it is active in the visible region (Yin *et al.*, 2015). Nanocomposites of g-C_3N_4 and TiO_2 have been used to photoreduce CO_2 to other hydrocarbons such as $CH_{4,}$ CO (Zhou *et al.*, 2014) and H_2 (Chai *et al.*, 2012). Therefore considering the work of (Slamet, *et al.*, 2009) and previous works done on g-C_3N_4 and TiO_2 nanocomposites, the focus of this research is to investigate the prospects of g-C_3N_4/(Cu/TiO_2) for photoreduction of CO_2 to CH_3OH. The doping with copped helps in creation of more active sites for adsorption of CO_2, (2) enables TiO_2 to absorb and utilize visible light and (3) creates a Schottky barrier, which promotes separation of electron and hole pairs hence inhibiting recombination (Slamet, *et al.*, 2009).

In conclusion, the yield of the product is of major concern in photocatalytic reduction of CO_2 and the yield depends on: - the type of photocatalyst, nature of the light used, reductant and type of reactor used. The nanocomposite synthesized (g-C_3N_4/(Cu/TiO_2) is expected to fulfill the material requirements to obtain a yield that is better than that of pure TiO_2. This is because the nanocomposite utilizes the unique properties of each of its constituents (g-C_3N_4, TiO_2 and Cu) to provide the necessary band structure required for effective charge separation, light absorption and utilization. It is expected that the use of NaOH as the reductant, two different light sources (UV and Visible) and the slurry type photoreactors would improve the yield of CH_3OH produced.

1.3 Problem Statement and Research Hypothesis

Though photoreduction of CO_2 to hydrocarbons is getting increased attention in research there are still certain limitations faced and the main challenges are low yield and selectivity of the products. To this end, the problems and possible solution approach are:

1. There is a need for a photocatalyst that is photo-stable, possess high light absorption and utilization efficiency, has high charge separation, inhibits recombination, absorbs in both the UV and visible region and has a large surface area to adsorb enough CO_2. The constituents of the $g{-}C_3N_4/(Cu/TiO_2)$ nanocomposite possess these characteristics hence it is expected these problems will be solved by synthesizing it.

2. The solubility of CO_2 in the reductant used dictates the amount of CO_2 available for the photocatalyst and the photoreduction process. A reductant that is environmentally benign, affordable and dissolves CO_2 very well is one of the focus of CO_2 photoreduction. The use of NaOH as a reductant would improve the solubility of CO_2 into the system and give the desired result during photo splitting as opposed to using pure water.

3. The selectivity of the product from photoreduction of CO_2 depends on the choice of dopant or co-catalyst used. For example, Pt. is known to possess a high affinity for H_2 and CH_4 during photoreduction of CO_2. Therefore, the type of co-catalyst to use is paramount. The use of Cu in the photoreduction of CO_2 is expected to give high selectivity for CH_3OH production.

4. The knowledge of how type of light affects the mechanism of CO_2 photoreduction is a topic of debate and research is focused on understanding more about this. The use of both UV and visible light in this research is expected to shed more light to this issue and give better understanding on the effect of light intensity.

1.4 Research Objective

The objectives of this research include: -

1. To synthesize and characterize copper and graphitic carbon nitride based TiO_2 nanocatalysts for CO_2 conversion to methanol;

2. To study and compare the performance of nanocatalysts for selective photocatalytic CO_2 conversion to methanol under UV and visible light irradiations;

3. To study the effect of operating parameters and propose reaction mechanisms for the catalyst having maximum yield and selectivity.

1.5 Research Scope

The research focus is summarized in detail. The photocatalysts to be used for the photoreduction process were synthesized i.e. ($g-C_3N_4$, $g-C_3N_4/TiO_2$, Cu/TiO_2, $Cu/g-C_3N_4$, $(Cu/g-C_3N_4)/TiO_2$, $g-C_3N_4/(Cu/TiO_2)$) using the appropriate methods. The characterization of the catalysts was carried out using the following technologies XRD, FTIR, FESEM, BET, XPS, TEM, UV-VIS and PL. These analysis were done to determine the crystalline nature, the organic and inorganic bands of functional groups, morphology, surface area, porosity and pore dimension, oxidative state, atomic structure and the formation of heterostructure, absorption region of each catalyst in the spectrum and identify the catalyst sample with the lowest PL emission intensity and recombination rate respectively. The catalysts were then used to photoreduce CO_2 to obtain CH_3OH using both UV &Visible light and their performances were compared based on the yield of CH_3OH. The catalyst with the optimum yield of methanol was used to study the operating parameters (time, % weight ratio and photostability test). After proper analysis and study of the results obtained, reaction mechanisms for both UV and Visible light were proposed.

1.6 Significance of Study

This study has immense contribution to researchers in photocatalysis, the scientific community and the public for the following reasons. Firstly, the research on the g-C_3N_4/(Cu/TiO_2) nanocomposite provides more insight and direction on the mechanism of composites during CO_2 photoreduction. In addition, the effect of type of light on the efficiency of photocatalysis can be better understood from this research. A photocatalyst that is photo-stable, has high charge separation and is environmentally benign has been introduced. The process of CO_2 utilization and conversion has been accomplished through this study.

1.7 Outline of Thesis

This thesis is divided into five chapters excluding all introductory pages, table of content and abstract. The first chapter (Chapter 1) contains 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, and characterization techniques 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.

REFERENCES

Abramowicz, D., Pradier, O., Pauw, L. D., Kinnaert, P., Mat, O., Surquin, M., Doutrelepont, J.-M., Vanherweghem, J.-L., Capel, P. and Vereerstraeten, P. (1994). High-dose glucocorticosteroids increase the procoagulant effects of OKT3. *Kidney international*. 46(6), 1596-1602.

Al-Ahmed, A. (2013). Metal doped TiO_2 photocatalysts for CO_2 photoreduction. *Proceedings of the 2013 Materials Science Forum*: Trans Tech Publ, 243-256.

Ali, K. A., Abdullah, A. Z. and Mohamed, A. R. (2015). Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review. *Renewable and Sustainable Energy Reviews*. 44, 508-518.

Ampelli, C., Passalacqua, R., Genovese, C., Perathoner, S., Centi, G., Montini, T., Gombac, V., Jaen, J. J. D. and Fornasiero, P. (2013). H_2 production by selective photo-dehydrogenation of ethanol in gas and liquid phase on CuO x/TiO_2 nanocomposites. *RSC Advances*. 3(44), 21776-21788.

Anpo, M., Ichihashi, Y., Takeuchi, M. and Yamashita, H. (1998). Design of unique titanium oxide photocatalysts by an advanced metal ion-implantation method and photocatalytic reactions under visible light irradiation. *Research on chemical intermediates*. 24(2), 143-149.

Anpo, M., Yamashita, H., Ichihashi, Y. and Ehara, S. (1995). Photocatalytic reduction of CO_2 with H_2O on various titanium oxide catalysts. *Journal of Electroanalytical Chemistry*. 396(1), 21-26.

Apaydin, D. H., Tordin, E., Portenkirchner, E., Aufischer, G., Schlager, S., Weichselbaumer, M., Oppelt, K. and Sariciftci, N. S. (2016). Photoelectrochemical Reduction of CO_2 Using Third-Generation Conjugated Polymers. *ChemistrySelect*. 1(6), 1156-1162.

Aruchamy, A., Aravamudan, G. and Subba Rao, G. (1982). Semiconductor based photoelectrochemical cells for solar energy conversion-An overview. *Bulletin of Materials Science*. 4(5), 483-526.

Bann, B. and Miller, S. A. (1958). Melamine and derivatives of melamine. *Chemical reviews*. 58(1), 131-172.

Bohren, C. F. and Huffman, D. R. (1983). Absorption and scattering by a sphere. *Absorption and Scattering of Light by Small Particles*. 82-129.

Chai, B., Peng, T., Mao, J., Li, K. and Zan, L. (2012). Graphitic carbon nitride (g-C_3N_4)-Pt-TiO_2 nanocomposite as an efficient photocatalyst for hydrogen production under visible light irradiation. *Phys Chem Chem Phys*. 14(48), 16745-16752.

Cheah, W. Y., Ling, T. C., Juan, J. C., Lee, D.-J., Chang, J.-S. and Show, P. L. (2016). Biorefineries of carbon dioxide: From carbon capture and storage (CCS) to bioenergies production. *Bioresource Technology*.

Chen, L., Zeng, X., Si, P., Chen, Y., Chi, Y., Kim, D.-H. and Chen, G. (2014). Gold nanoparticle-graphite-like C_3N_4 nanosheet nanohybrids used for electrochemiluminescent immunosensor. *Analytical chemistry*. 86(9), 4188-4195.

Chen, R., Lu, M.-C., Srinivasan, V., Wang, Z., Cho, H. H. and Majumdar, A. (2009). Nanowires for enhanced boiling heat transfer. *Nano letters*. 9(2), 548-553.

Cowan, A. J., Tang, J., Leng, W., Durrant, J. R. and Klug, D. R. (2010). Water splitting by nanocrystalline TiO_2 in a complete photoelectrochemical cell exhibits efficiencies limited by charge recombination. *The Journal of Physical Chemistry C*. 114(9), 4208-4214.

Cybula, A., Klein, M., Zieli ska-Jurek, A., Janczarek, M. and Zaleska, A. (2012). Carbon dioxide photoconversion. The effect of titanium dioxide immobilization conditions and photocatalyst type. *Physicochemical Problems of Mineral Processing*. 48(1), 159-167.

Das, A., Khan, F., Sampath, A. and Su, H.-J. (2002). Adaptive, asynchronous incremental redundancy (A 2 IR) with fixed transmission time intervals (TTI) for HSDPA. *Proceedings of the 2002 Personal, Indoor and Mobile Radio Communications, 2002. The 13th IEEE International Symposium on*: IEEE, 1083-1087.

Daud, M. and Rahman, A. (2013). Photo-Catalytic Reduction of Carbon Dioxide Over Alumina Doped Titanium Dioxide Catalyst.

David, A. O., Tahir, M. and Amin, N. A. S. (2015). Copper modified TiO_2 and g-C_3N_4 catalysts for photoreduction of CO_2 to methanol using different reaction mediums. *Malaysian Journal of Fundamental and Applied Sciences*. 11(3).

Dementjev, A., De Graaf, A., Van de Sanden, M., Maslakov, K., Naumkin, A. and Serov, A. (2000). X-ray photoelectron spectroscopy reference data for identification of the C_3N_4 phase in carbon–nitrogen films. *Diamond and related materials*. 9(11), 1904-1907.

Dey, G., Belapurkar, A. and Kishore, K. (2004). Photo-catalytic reduction of carbon dioxide to methane using TiO_2 as suspension in water. *Journal of Photochemistry and photobiology A: Chemistry*. 163(3), 503-508.

Di Paola, A., García-López, E., Marcì, G. and Palmisano, L. (2012). A survey of photocatalytic materials for environmental remediation. *Journal of hazardous materials*. 211, 3-29.

Ding, Z., Chen, X., Antonietti, M. and Wang, X. (2011). Synthesis of transition metal-modified carbon nitride polymers for selective hydrocarbon oxidation. *ChemSusChem*. 4(2), 274-281.

Dong, G. and Zhang, L. (2012). Porous structure dependent photoreactivity of graphitic carbon nitride under visible light. *Journal of Materials Chemistry*. 22(3), 1160-1166.

Dong, L., Li, M., Zhao, M., Feng, J., Han, Y., Deng, J., Li, X., Li, D. and Sun, X. (2014). Hydrothermal synthesis of mixed crystal phases TiO_2–reduced graphene oxide nanocomposites with small particle size for lithium ion batteries. *international journal of hydrogen energy*. 39(28), 16116-16122.

Dufour, A. (2016). *Thermochemical Conversion of Biomass for the Production of Energy and Chemicals*. John Wiley & Sons.

Fox, M. A. and Dulay, M. T. (1993). Heterogeneous photocatalysis. *Chemical reviews*. 93(1), 341-357.

Ganesh, I. (2013). Conversion of Carbon Dioxide into Several Potential Chemical Commodities Following Different Pathways - A Review. *Materials Science Forum*. 764, 1-82.

Gao, J., Wang, J., Qian, X., Dong, Y., Xu, H., Song, R., Yan, C., Zhu, H., Zhong, Q. and Qian, G. (2015). One-pot synthesis of copper-doped graphitic carbon nitride nanosheet by heating Cu–melamine supramolecular network and its enhanced visible-light-driven photocatalysis. *Journal of Solid State Chemistry*. 228, 60-64.

Gao, T., Meng, G., Wang, Y., Sun, S. and Zhang, L. (2002). Electrochemical synthesis of copper nanowires. *Journal of Physics: Condensed Matter*. 14(3), 355.

Ghadimkhani, G., de Tacconi, N. R., Chanmanee, W., Janaky, C. and Rajeshwar, K. (2013). Efficient solar photoelectrosynthesis of methanol from carbon dioxide using hybrid CuO–Cu_2O semiconductor nanorod arrays. *Chemical Communications*. 49(13), 1297-1299.

Graham, D. J., Orquin, J. L. and Visschers, V. H. (2012). Eye tracking and nutrition label use: A review of the literature and recommendations for label enhancement. *Food Policy*. 37(4), 378-382.

Grebenshchikov, S. Y. (2016). Photochemistry of carbon dioxide from first principles: Application to photoabsorption of hot CO_2. *Journal of CO_2 Utilization*.

Gribb, A. A. and Banfield, J. F. (1997). Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO_2. *American Mineralogist*. 82(7), 717-728.

Guo, H., Lin, N., Chen, Y., Wang, Z., Xie, Q., Zheng, T., Gao, N., Li, S., Kang, J. and Cai, D. (2013). Copper nanowires as fully transparent conductive electrodes. *Scientific reports*. 3.

Gusain, R., Kumar, P., Sharma, O. P., Jain, S. L. and Khatri, O. P. (2016). Reduced graphene oxide–CuO nanocomposites for photocatalytic conversion of CO_2 into methanol under visible light irradiation. *Applied Catalysis B: Environmental*. 181, 352-362.

Hafner, S. and Nagel, S. (1983). The electric field gradient at the position of copper in Cu_2O and electronic charge density analysis by means of K-factors. *Physics and Chemistry of Minerals*. 9(1), 19-22.

Halmann, M. (1978). Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells.

He, Y., Wang, Y., Zhang, L., Teng, B. and Fan, M. (2015). High-efficiency conversion of CO_2 to fuel over ZnO/g-C_3N_4 photocatalyst. *Applied Catalysis B: Environmental*. 168-169, 1-8.

Hou, Y., Wen, Z., Cui, S., Guo, X. and Chen, J. (2013). Constructing 2D Porous Graphitic C_3N_4 Nanosheets/Nitrogen-Doped Graphene/Layered MoS_2 Ternary

Nanojunction with Enhanced Photoelectrochemical Activity. *Advanced Materials*. 25(43), 6291-6297.

Hsu, C.-L., Chang, S.-J., Lin, Y.-R., Li, P.-C., Lin, T.-S., Tsai, S.-Y., Lu, T.-H. and Chen, I.-C. (2005). Ultraviolet photodetectors with low temperature synthesized vertical ZnO nanowires. *Chemical Physics Letters*. 416(1), 75-78.

Huang, Q., Kang, F., Liu, H., Li, Q. and Xiao, X. (2013). Highly aligned $Cu_2O/CuO/TiO_2$ core/shell nanowire arrays as photocathodes for water photoelectrolysis. *Journal of Materials Chemistry A*. 1(7), 2418-2425.

Indrakanti, V. P., Kubicki, J. D. and Schobert, H. H. (2009). Photoinduced activation of CO_2 on Ti-based heterogeneous catalysts: current state, chemical physics-based insights and outlook. *Energy & Environmental Science*. 2(7), 745-758.

Izumi, Y. (2013). Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond. *Coordination Chemistry Reviews*. 257(1), 171-186.

Jiang, Z., Xiao, T., Kuznetsov, V. L. and Edwards, P. P. (2010). Turning carbon dioxide into fuel. *Philos Trans A Math Phys Eng Sci*. 368(1923), 3343-3364.

Kaneco, S., Kurimoto, H., Ohta, K., Mizuno, T. and Saji, A. (1997). Photocatalytic reduction of CO_2 using TiO_2 powders in liquid CO_2 medium. *Journal of Photochemistry and Photobiology A: Chemistry*. 109(1), 59-63.

Kaneco, S., Kurimoto, H., Shimizu, Y., Ohta, K. and Mizuno, T. (1999). Photocatalytic reduction of CO_2 using TiO_2 powders in supercritical fluid CO_2. *Energy*. 24(1), 21-30.

Kaneco, S., Shimizu, Y., Ohta, K. and Mizuno, T. (1998). Photocatalytic reduction of high pressure carbon dioxide using TiO_2 powders with a positive hole scavenger. *Journal of Photochemistry and Photobiology A: Chemistry*. 115(3), 223-226.

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K. (1999). Titania nanotubes prepared by chemical processing. *Advanced Materials*. 11(15), 1307-1311.

Kevin, M., Ong, W., Lee, G. and Ho, G. (2011). Formation of hybrid structures: copper oxide nanocrystals templated on ultralong copper nanowires for open network sensing at room temperature. *Nanotechnology*. 22(23), 235701.

Khan, S. U., Al-Shahry, M. and Ingler, W. B. (2002). Efficient photochemical water splitting by a chemically modified n-TiO_2. *science*. 297(5590), 2243-2245.

Khatri, R. A., Chuang, S. S., Soong, Y. and Gray, M. (2005). Carbon dioxide capture by diamine-grafted SBA-15: A combined Fourier transform infrared and mass spectrometry study. *Industrial & Engineering Chemistry Research*. 44(10), 3702-3708.

Kočí, K., Matějka, V., Kovář, P., Lacný, Z. and Obalová, L. (2011). Comparison of the pure TiO_2 and kaolinite/TiO_2 composite as catalyst for CO_2 photocatalytic reduction. *Catalysis Today*. 161(1), 105-109.

Kočí, K., Obalova, L. and Lacný, Z. (2008). Photocatalytic reduction of CO_2 over TiO2 based catalysts. *Chemical Papers*. 62(1), 1-9.

Kočí, K., Obalová, L., Matějová, L., Plachá, D., Lacný, Z., Jirkovský, J. and Šolcová, O. (2009). Effect of TiO_2 particle size on the photocatalytic reduction of CO_2. *Applied Catalysis B: Environmental*. 89(3-4), 494-502.

Kohno, Y., Hayashi, H., Takenaka, S., Tanaka, T., Funabiki, T. and Yoshida, S. (1999). Photo-enhanced reduction of carbon dioxide with hydrogen over Rh/TiO_2. *Journal of Photochemistry and photobiology A: Chemistry*. 126(1), 117-123.

Krejčíková, S., Matějová, L., Kočí, K., Obalová, L., Matěj, Z., Čapek, L. and Šolcová, O. (2012). Preparation and characterization of Ag-doped crystalline titania for photocatalysis applications. *Applied Catalysis B: Environmental*. 111, 119-125.

Kroger, H. (1964). ELECTRON-STIMULATED PIEZOELECTRIC NONLINEAR ACOUSTIC EFFECT IN CdS. *Applied Physics Letters*. 4(11), 190-192.

Ku, Y., Lee, W.-H. and Wang, W.-Y. (2004). Photocatalytic reduction of carbonate in aqueous solution by UV/TiO_2 process. *Journal of Molecular Catalysis A: Chemical*. 212(1), 191-196.

LaTempa, T. J., Rani, S., Bao, N. and Grimes, C. A. (2012). Generation of fuel from CO 2 saturated liquids using a p-Si nanowire‖ n-TiO_2 nanotube array photoelectrochemical cell. *Nanoscale*. 4(7), 2245-2250.

Li, H., Dai, J., Li, J., Zhang, S., Zhou, J., Zhang, L., Chu, W., Chen, D., Zhao, H. and Yang, J. (2010). Electronic structures and magnetic properties of GaN sheets and nanoribbons. *The Journal of Physical Chemistry C*. 114(26), 11390-11394.

Li, H., Zhang, X. and MacFarlane, D. R. (2015). Carbon Quantum Dots/Cu2O Heterostructures for Solar-Light-Driven Conversion of CO_2 to Methanol. *Advanced Energy Materials*. 5(5).

Li, L., Shi, Z., Gao, B., Hu, X. and Wang, Z. (2016). Electrochemical conversion of CO_2 to carbon and oxygen in LiCl–Li_2O melts. *Electrochimica Acta*. 190, 655-658.

Li, X., Liu, H., Luo, D., Li, J., Huang, Y., Li, H., Fang, Y., Xu, Y. and Zhu, L. (2012). Adsorption of CO_2 on heterostructure CdS (Bi_2S_3)/TiO_2 nanotube photocatalysts and their photocatalytic activities in the reduction of CO_2 to methanol under visible light irradiation. *Chemical Engineering Journal*. 180, 151-158.

Liang, H. P., Zhang, H. M., Hu, J. S., Guo, Y. G., Wan, L. J. and Bai, C. L. (2004). Pt hollow nanospheres: facile synthesis and enhanced electrocatalysts. *Angewandte Chemie*. 116(12), 1566-1569.

Liao, G., Chen, S., Quan, X., Yu, H. and Zhao, H. (2012). Graphene oxide modified gC_3N_4 hybrid with enhanced photocatalytic capability under visible light irradiation. *Journal of Materials Chemistry*. 22(6), 2721-2726.

Lide, D. R. (2005). Physical constants of organic compounds. *CRC Handbook of Chemistry and Physics*. 89, 3-1.

Lin, Y., Yuan, G., Liu, R., Zhou, S., Sheehan, S. W. and Wang, D. (2011). Semiconductor nanostructure-based photoelectrochemical water splitting: A brief review. *Chemical Physics Letters*. 507(4), 209-215.

Linsebigler, A. L., Lu, G. and Yates Jr, J. T. (1995). Photocatalysis on TiO2 surfaces: principles, mechanisms, and selected results. *Chemical reviews*. 95(3), 735-758.

Liou, P.-Y., Chen, S.-C., Wu, J. C., Liu, D., Mackintosh, S., Maroto-Valer, M. and Linforth, R. (2011). Photocatalytic CO_2 reduction using an internally illuminated monolith photoreactor. *Energy & Environmental Science*. 4(4), 1487-1494.

Liu, E., Kang, L., Wu, F., Sun, T., Hu, X., Yang, Y., Liu, H. and Fan, J. (2014). Photocatalytic reduction of CO_2 into methanol over Ag/TiO_2 nanocomposites enhanced by surface plasmon resonance. *Plasmonics*. 9(1), 61-70.

Lo, C.-C., Hung, C.-H., Yuan, C.-S. and Wu, J.-F. (2007). Photoreduction of carbon dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a circulated photocatalytic reactor. *Solar Energy Materials and Solar Cells*. 91(19), 1765-1774.

Lofrano, G., Rizzo, L., Grassi, M. and Belgiorno, V. (2009). Advanced oxidation of catechol: A comparison among photocatalysis, Fenton and photo-Fenton processes. *Desalination*. 249(2), 878-883.

Lotsch, B. V. and Schnick, W. (2005). Thermal Conversion of Guanylurea Dicyanamide into Graphitic Carbon Nitride via Prototype CN X Precursors. *Chemistry of materials*. 17(15), 3976-3982.

Lueker, T. J., Dickson, A. G. and Keeling, C. D. (2000). Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry*. 70(1), 105-119.

Ma, Y., Wang, X., Jia, Y., Chen, X., Han, H. and Li, C. (2014). Titanium dioxide-based nanomaterials for photocatalytic fuel generations. *Chem Rev*. 114(19), 9987-10043.

Maginn, E. J. (2010). What to Do with CO_2. *The Journal of Physical Chemistry Letters*. 1(24), 3478-3479.

Mao, J., Peng, T., Zhang, X., Li, K., Ye, L. and Zan, L. (2013). Effect of graphitic carbon nitride microstructures on the activity and selectivity of photocatalytic CO_2 reduction under visible light. *Catalysis Science & Technology*. 3(5), 1253.

Marszewski, M., Cao, S., Yu, J. and Jaroniec, M. (2015). Semiconductor-based photocatalytic CO_2 conversion. *Mater. Horiz.* 2(3), 261-278.

Martin-Gil, J., Martin-Gil, F., Moran, E., Miki-Yoshida, M., Martínez, L. and José-Yacamán, M. (1995). Synthesis of low density and high hardness carbon spheres containing nitrogen and oxygen. *Acta metallurgica et materialia*. 43(3), 1243-1247.

Mizuno, T., Adachi, K., Ohta, K. and Saji, A. (1996). Effect of CO_2 pressure on photocatalytic reduction of CO_2 using TiO_2 in aqueous solutions. *Journal of Photochemistry and Photobiology A: Chemistry*. 98(1), 87-90.

Molares, M. T., Buschmann, V., Dobrev, D., Neumann, R., Scholz, R., Schuchert, I. U. and Vetter, J. (2001). Single-crystalline copper nanowires produced by electrochemical deposition in polymeric ion track membranes. *Adv. Mater*. 13(1), 62-65.

Moritis, G. (2004). Study shows downhole water separation languishes. *Oil & gas journal*. 102(47), 44-45.

Murgatroyd, C. and Hodges, P. (2001). Building on MARS. *HYDROCARBON ENGINEERING*. 6(8), 41-46.

Nakaoka, K., Ueyama, J. and Ogura, K. (2004). Photoelectrochemical Behavior of Electrodeposited CuO and Cu_2O Thin Films on Conducting Substrates. *Journal of the Electrochemical Society*. 151(10), C661-C665.

Nasution, H., Purnama, E., Kosela, S. and Gunlazuardi, J. (2005). Photocatalytic reduction of CO on copper-doped Titania catalysts prepared by improved-impregnation method. *Catalysis Communications*. 6(5), 313-319.

Neaţu, S. t., Maciá-Agulló, J. A., Concepción, P. and Garcia, H. (2014). Gold–copper nanoalloys supported on TiO_2 as photocatalysts for CO_2 reduction by water. *Journal of the American Chemical Society*. 136(45), 15969-15976.

Nguyen, T.-V. and Wu, J. C. (2008). Photoreduction of CO_2 in an optical-fiber photoreactor: effects of metals addition and catalyst carrier. *Applied Catalysis A: General*. 335(1), 112-120.

Ni, M., Leung, M. K., Leung, D. Y. and Sumathy, K. (2007). A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *Renewable and Sustainable Energy Reviews*. 11(3), 401-425.

Nishimura, A., Mitsui, G., Hirota, M. and Hu, E. (2010). CO_2 Reforming Performance and Visible Light Responsibility of Cr-Doped TiO_2 Prepared by Sol-Gel and Dip-Coating Method. *International Journal of Chemical Engineering*. 2010.

Niu, P., Zhang, L., Liu, G. and Cheng, H. M. (2012). Graphene Like Carbon Nitride Nanosheets for Improved Photocatalytic Activities. *Advanced Functional Materials*. 22(22), 4763-4770.

Ola, O. and Maroto-Valer, M. M. (2015). Review of material design and reactor engineering on TiO_2 photocatalysis for CO_2 reduction. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 24, 16-42.

Olah, G., Goeppert, A. and Prakash, G. S. (2006). Beyond Gas and Oil: The Methanol Economy. Wiley-VCH, New York.

Olah, G. A., Goeppert, A. and Prakash, G. S. (2008). Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *The Journal of organic chemistry*. 74(2), 487-498.

Olah, G. A., Prakash, G. S., Sommer, J. and Molnar, A. (2009). *Superacid chemistry*. John Wiley & Sons.

Ozcan, O., Yukruk, F., Akkaya, E. and Uner, D. (2007). Dye sensitized artificial photosynthesis in the gas phase over thin and thick TiO_2 films under UV and visible light irradiation. *Applied Catalysis B: Environmental*. 71(3), 291-297.

Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. and Friend, C. M. (2013). Sequential photo-oxidation of methanol to methyl formate on TiO_2 (110). *Journal of the American Chemical Society*. 135(2), 574-577.

Pierantozzi, R. (1993). Carbon Monoxide. *Kirk-Othmer encyclopedia of chemical technology*.

Prasad, D. R., Rahmat, N. S. B., Ong, H. R., Cheng, C. K., Khan, M. R. and Sathiyamoorthy, D. (2016). Preparation and Characterization of Photocatalyst for the Conversion of Carbon Dioxide to Methanol. *World Academy of Science, Engineering and Technology, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*. 10(5), 464-467.

Qin, S., Xin, F., Liu, Y., Yin, X. and Ma, W. (2011). Photocatalytic reduction of CO_2 in methanol to methyl formate over CuO–TiO_2 composite catalysts. *Journal of colloid and interface science*. 356(1), 257-261.

Qu, J., Zhang, X., Wang, Y. and Xie, C. (2005). Electrochemical reduction of CO_2 on RuO_2/TiO_2 nanotubes composite modified Pt electrode. *Electrochimica Acta*. 50(16), 3576-3580.

Raja, K., Smith, Y., Kondamudi, N., Manivannan, A., Misra, M. and Subramanian, V. R. (2011). CO_2 photoreduction in the liquid phase over Pd-supported on TiO_2 nanotube and bismuth titanate photocatalysts. *Electrochemical and Solid-State Letters*. 14(5), F5-F8.

Rajalakshmi, K. (2011). *Photocatalytic reduction of carbon dioxide in conjunction with decomposition of water on oxide semiconductor surfaces*, INDIAN INSTITUTE OF TECHNOLOGY, MADRAS CHENNAI.

Reli, M., Šihor, M., Kočí, K., Praus, P., Kozák, O. and Obalová, L. (2012). Influence of reaction medium on CO_2 photocatalytic reduction yields over.

Ridley, B. K. (2013). *Quantum processes in semiconductors*. Oxford University Press.

Romm, J. J. (2004). *The hype about hydrogen: fact and fiction in the race to save the climate*. Island Press.

Sakata, Y., Yoshimoto, K., Kawaguchi, K., Imamura, H. and Higashimoto, S. (2011). Preparation of a semiconductive compound obtained by the pyrolysis of urea under N_2 and the photocatalytic property under visible light irradiation. *Catalysis Today*. 161(1), 41-45.

Salvi, A. M., Langerame, F., Macchia, A., Sammartino, M. P. and Tabasso, M. L. (2012). XPS characterization of (copper-based) coloured stains formed on limestone surfaces of outdoor Roman monuments. *Chem. Cent. J*. 6(suppl 2), 510.

Schulte, K. L., DeSario, P. A. and Gray, K. A. (2010). Effect of crystal phase composition on the reductive and oxidative abilities of TiO_2 nanotubes under UV and visible light. *Applied Catalysis B: Environmental*. 97(3), 354-360.

Shakhashiri, B. (2008). The Chemistry of Autumn Colors. *Science Is Fun. Retrieved from the World Wide Web on*. 18.

Shi, J., Hara, Y., Sun, C., Anderson, M. A. and Wang, X. (2011). Three-dimensional high-density hierarchical nanowire architecture for high-performance photoelectrochemical electrodes. *Nano letters*. 11(8), 3413-3419.

Slamet, H. W. N., Purnama, E., Riyani, K. and Gunlazuardi, J. (2009). Effect of copper species in a photocatalytic synthesis of methanol from carbon dioxide over copper-doped titania catalysts. *World Appl Sci J*. 6(1), 112.

Song, I. K., Yu, W. J., Cho, Y. S., Choi, G. S. and Kim, D. (2004). The determining factors for the growth mode of carbon nanotubes in the chemical vapour deposition process. *Nanotechnology*. 15(10), S590.

Stolaroff, J. (2013). Carbonate solutions for carbon capture: A summary. Lawrence Livermore National Laboratory (LLNL), Livermore, CA.

Stroyuk, A., Kryukov, A., Kuchmii, S. Y. and Pokhodenko, V. (2009). Semiconductor photocatalytic systems for the production of hydrogen by the action of visible light. *Theoretical and Experimental Chemistry*. 45(4), 209-233.

Sun, J.-X., Yuan, Y.-P., Qiu, L.-G., Jiang, X., Xie, A.-J., Shen, Y.-H. and Zhu, J.-F. (2012). Fabrication of composite photocatalyst gC_3N_4–ZnO and enhancement of photocatalytic activity under visible light. *Dalton Transactions*. 41(22), 6756-6763.

Sun, S., Wang, W., Zhang, L., Shang, M. and Wang, L. (2009). Ag@C core/shell nanocomposite as a highly efficient plasmonic photocatalyst. *Catalysis Communications*. 11(4), 290-293.

Tahir, M. and Amin, N. S. (2013). Advances in visible light responsive titanium oxide-based photocatalysts for CO_2 conversion to hydrocarbon fuels. *Energy Conversion and Management*. 76, 194-214.

Tahir, M. and Tahir, B. (2016). Dynamic photocatalytic reduction of CO_2 to CO in a honeycomb monolith reactor loaded with Cu and N doped TiO_2 nanocatalysts. *Applied Surface Science*.

Tan, J. Z., Fernández, Y., Liu, D., Maroto-Valer, M., Bian, J. and Zhang, X. (2012). Photoreduction of CO_2 using copper-decorated TiO_2 nanorod films with localized surface plasmon behavior. *Chemical Physics Letters*. 531, 149-154.

Tan, S. S., Zou, L. and Hu, E. (2007). Photosynthesis of hydrogen and methane as key components for clean energy system. *Science and technology of advanced materials*. 8(1), 89-92.

Tan, X., Fang, M. and Wang, X. (2008). Preparation of TiO_2/multiwalled carbon nanotube composites and their applications in photocatalytic reduction of Cr (VI) study. *Journal of nanoscience and nanotechnology*. 8(11), 5624-5631.

Thomann, I., Pinaud, B. A., Chen, Z., Clemens, B. M., Jaramillo, T. F. and Brongersma, M. L. (2011). Plasmon enhanced solar-to-fuel energy conversion. *Nano letters*. 11(8), 3440-3446.

Thomas, A., Fischer, A., Goettmann, F., Antonietti, M., Müller, J.-O., Schlögl, R. and Carlsson, J. M. (2008). Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts. *Journal of Materials Chemistry*. 18(41), 4893.

Truong, Q. D., Liu, J.-Y., Chung, C.-C. and Ling, Y.-C. (2012). Photocatalytic reduction of CO_2 on $FeTiO_3$/TiO_2 photocatalyst. *Catalysis Communications*. 19, 85-89.

Tseng, I.-H., Chang, W.-C. and Wu, J. C. (2002). Photoreduction of CO_2 using sol–gel derived titania and titania-supported copper catalysts. *Applied Catalysis B: Environmental*. 37(1), 37-48.

Tseng, I.-H., Wu, J. C. and Chou, H.-Y. (2004). Effects of sol–gel procedures on the photocatalysis of Cu/TiO_2 in CO_2 photoreduction. *Journal of Catalysis*. 221(2), 432-440.

Valden, M., Pak, S., Lai, X. and Goodman, D. (1998). Structure sensitivity of CO oxidation over model Au/TiO_2 catalysts. *Catalysis Letters*. 56(1), 7-10.

Varghese, O. K., Paulose, M., LaTempa, T. J. and Grimes, C. A. (2009). High-rate solar photocatalytic conversion of CO_2 and water vapor to hydrocarbon fuels. *Nano letters*. 9(2), 731-737.

Vijayan, B. K., Dimitrijevic, N. M., Wu, J. and Gray, K. A. (2010). The effects of Pt doping on the structure and visible light photoactivity of titania nanotubes. *The Journal of Physical Chemistry C*. 114(49), 21262-21269.

Wang, H., Yuan, X., Wu, Y., Zeng, G., Chen, X., Leng, L. and Li, H. (2015a). Synthesis and applications of novel graphitic carbon nitride/metal-organic frameworks mesoporous photocatalyst for dyes removal. *Applied Catalysis B: Environmental*. 174, 445-454.

Wang, J. and Zhang, W.-D. (2012). Modification of TiO 2 nanorod arrays by graphite-like g-C_3N_4 with high visible light photoelectrochemical activity. *Electrochimica Acta*. 71, 10-16.

Wang, K., Li, Q., Liu, B., Cheng, B., Ho, W. and Yu, J. (2015b). Sulfur-doped g-C3N4 with enhanced photocatalytic CO_2-reduction performance. *Applied Catalysis B: Environmental*. 176-177, 44-52.

Wang, X., Li, Z., Shi, J. and Yu, Y. (2014). One-dimensional titanium dioxide nanomaterials: nanowires, nanorods, and nanobelts. *Chemical reviews*. 114(19), 9346-9384.

Wang, X., Maeda, K., Thomas, A., Takanabe, K., Xin, G., Carlsson, J. M., Domen, K. and Antonietti, M. (2009). A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nature materials*. 8(1), 76-80.

Wang, Y., Wang, X. and Antonietti, M. (2012). Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: from photochemistry to multipurpose catalysis to sustainable chemistry. *Angew Chem Int Ed Engl*. 51(1), 68-89.

Wang, Y., Wang, Y. and Gao, Y. (2010). Photocatalytic H_2 evolution from water in the presence of carbon dioxide over NiO/$Ca_2Fe_2O_5$. *Reaction Kinetics, Mechanisms and Catalysis*. 99(2), 485-491.

Winner, B., Jappelli, R., Maji, S. K., Desplats, P. A., Boyer, L., Aigner, S., Hetzer, C., Loher, T., Vilar, M. and Campioni, S. (2011). In vivo demonstration that -synuclein oligomers are toxic. *Proceedings of the National Academy of Sciences*. 108(10), 4194-4199.

Woolerton, T. W., Sheard, S., Reisner, E., Pierce, E., Ragsdale, S. W. and Armstrong, F. A. (2010). Efficient and clean photoreduction of CO_2 to CO by enzymemodified TiO_2 nanoparticles using visible light. *Journal of the American Chemical Society*. 132(7), 2132-2133.

Wu, J. C., Lin, H.-M. and Lai, C.-L. (2005). Photo reduction of CO_2 to methanol using optical-fiber photoreactor. *Applied Catalysis A: General*. 296(2), 194-200.

Xie, T.-f., Wang, D.-j., Zhu, L.-j., Li, T.-j. and Xu, Y.-j. (2001). Application of surface photovoltage technique in photocatalysis studies on modified TiO_2 photo-catalysts for photo-reduction of CO_2. *Materials chemistry and physics*. 70(1), 103-106.

Xu, X., Liu, G., Randorn, C. and Irvine, J. T. (2011). gC_3N_4 coated $SrTiO_3$ as an efficient photocatalyst for H_2 production in aqueous solution under visible light irradiation. *international journal of hydrogen energy*. 36(21), 13501-13507.

Yadav, V. and Purkait, M. (2016). Concurrent electrochemical CO_2 reduction to HCOOH and methylene blue removal on metal electrodes. *RSC Advances*. 6(47), 40916-40922.

Yan, H. and Yang, H. (2011). TiO_2–gC_3N_4 composite materials for photocatalytic H_2 evolution under visible light irradiation. *Journal of alloys and compounds*. 509(4), L26-L29.

Yan, R., Gargas, D. and Yang, P. (2009). Nanowire photonics. *Nature Photonics*. 3(10), 569-576.

Yang, C.-C., Yu, Y.-H., van der Linden, B., Wu, J. C. and Mul, G. (2010). Artificial photosynthesis over crystalline TiO_2-based catalysts: Fact or fiction? *Journal of the American Chemical Society*. 132(24), 8398-8406.

Yang, H.-C., Lin, H.-Y., Chien, Y.-S., Wu, J. C.-S. and Wu, H.-H. (2009). Mesoporous TiO_2/SBA-15, and Cu/TiO_2/SBA-15 composite photocatalysts for photoreduction of CO_2 to methanol. *Catalysis letters*. 131(3-4), 381-387.

Ye, S., Rathmell, A. R., Chen, Z., Stewart, I. E. and Wiley, B. J. (2014). Metal nanowire networks: the next generation of transparent conductors. *Advanced Materials*. 26(39), 6670-6687.

Yin, J.-Z., Xu, Q.-Q. and Wang, A.-Q. (2009). Controlled growth of copper nanoparticles and nanorods in the channels of SBA-15 by supercritical fluid deposition. *Chemical Engineering Communications*. 197(4), 627-632.

Yin, S., Han, J., Zhou, T. and Xu, R. (2015). Recent progress in g-C_3N_4 based low cost photocatalytic system: activity enhancement and emerging applications. *Catal. Sci. Technol.* 10.1039/c5cy00938c.

Yoong, L., Chong, F. K. and Dutta, B. K. (2009). Development of copper-doped TiO_2 photocatalyst for hydrogen production under visible light. *Energy*. 34(10), 1652-1661.

Yu, K.-P., Yu, W.-Y., Kuo, M.-C., Liou, Y.-C. and Chien, S.-H. (2008). Pt/titania-nanotube: A potential catalyst for CO_2 adsorption and hydrogenation. *Applied Catalysis B: Environmental*. 84(1), 112-118.

Zhang, J., Sun, J., Liu, W., Shi, S., Sun, H. and Guo, J. (2005). Synthesis of copper nanowires under a direct current electric field. *Nanotechnology*. 16(10), 2030.

Zhang, Q.-H., Han, W.-D., Hong, Y.-J. and Yu, J.-G. (2009). Photocatalytic reduction of CO_2 with H_2O on Pt-loaded TiO_2 catalyst. *Catalysis Today*. 148(3), 335-340.

Zhao, C., Chen, X. and Zhao, C. (2009). Effect of crystal structure on CO_2 capture characteristics of dry potassium-based sorbents. *Chemosphere*. 75(10), 1401-1404.

Zhao, N., Wang, G., Huang, Y., Wang, B., Yao, B. and Wu, Y. (2008). Preparation of nanowire arrays of amorphous carbon nanotube-coated single crystal SnO2. *Chemistry of Materials*. 20(8), 2612-2614.

Zhao, Y. and Burda, C. (2012). Development of plasmonic semiconductor nanomaterials with copper chalcogenides for a future with sustainable energy materials. *Energy & Environmental Science*. 5(2), 5564-5576.

Zhou, D.-D., He, C.-T., Liao, P.-Q., Xue, W., Zhang, W.-X., Zhou, H.-L., Zhang, J.-P. and Chen, X.-M. (2013). A flexible porous Cu (ii) bis-imidazolate framework with ultrahigh concentration of active sites for efficient and recyclable CO_2 capture. *Chemical Communications*. 49(100), 11728-11730.

Zhou, S., Liu, Y., Li, J., Wang, Y., Jiang, G., Zhao, Z., Wang, D., Duan, A., Liu, J. and Wei, Y. (2014). Facile in situ synthesis of graphitic carbon nitride (g-C_3N_4)-N-TiO_2 heterojunction as an efficient photocatalyst for the selective photoreduction of CO_2 to CO. *Applied Catalysis B: Environmental*. 158-159, 20-29.