UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF VISIBLE LIGHT ACTIVE COPPER-LOADED BISMUTH VANADATE PHOTOCATALYST

WAN TZE PENG

SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF VISIBLE LIGHT ACTIVE COPPER-LOADED BISMUTH VANADATE PHOTOCATALYST

By

WAN TZE PENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the degree of Master of Science

March 2016

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF VISIBLE LIGHT ACTIVE COPPER-LOADED BISMUTH VANADATE PHOTOCATALYST

By

WAN TZE PENG

March 2016

Chairman: Associate Prof. Abdul Halim Bin Abdullah, PhD

Faculty: Science

The intense rise of wastes production in the industrial field due to rapid industrialization had brought more concern and interest in the development of wastewater treatment technologies in the country. The aim of this study is to synthesize simple, high efficiency and environment-friendly photocatalyst with easy and affordable photodegradation experiments in degrading dye. In this study, a series of bismuth(III) vanadate ($BiVO_4$) photocatalysts were prepared via precipitation method and a series of Cu-loaded $BiVO_4$ (Cu-$BiVO_4$) photocatalysts were prepared via impregnation method.

XRD analysis showed that tetragonal phase of $BiVO_4$ was formed during precipitation process and the phase transformation from tetragonal to monoclinic phase of $BiVO_4$ was completed at temperature 450 °C after 4 hours of calcination in air. The crystallite size of the synthesized photocatalysts ranging from 25.8 to 51.1 nm. The synthesized photocatalysts were spherical in shape, as observed in FESEM images, with surface area from 0.2 to 0.8 m^2g^{-1}. The particle size of the photocatalysts obtained via TEM, was in the range of 34.1 to 60.6 nm. Result from UV/Vis DRS indicated that band gap energy of $BiVO_4$ had increased due to copper loading. The presence of copper in the Cu-$BiVO_4$ photocatalysts was justified by result of AAS.

Photocatalytic degradation efficiency of the $BiVO_4$ and Cu-$BiVO_4$ photocatalysts was evaluated by degrading methylene blue (MB) dye under visible-light irradiation. The optimum conditions of the photocatalytic degradation were based on parameters. Among the undoped $BiVO_4$ photocatalyst, sample calcined at 550 °C for 1 hour demonstrated the highest photocatalytic degradation efficiency. Highest removal percentage of MB dye solution at initial concentration of 10 ppm and initial pH at 8,

was achieved by loading 1.0 g of $BiVO_4$ in the photocatalytic degradation experiment, under 18W fluorescent light irradiation at room temperature.

The photocatalytic degradation efficiency of $BiVO_4$ photocatalyst was enhanced by doping copper (Cu). 1 wt% Cu-$BiVO_4$ was found to exhibit the highest photocatalytic degradation efficiency. The percentage removal of MB dye solution at initial concentration of 10 ppm and initial pH at 10, approached 99.57%, when 0.8 g of 1 wt% Cu-$BiVO_4$ was loaded in the photocatalytic degradation experiment, under 18W fluorescent light irradiation at room temperature. The photocatalytic degradation of MB dye in this study followed first order kinetics.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS, PENCIRIAN DAN PRESTASI FOTOMANGKIN CAHAYA NAMPAK BISMUT VANADAT DIMUATKAN DENGAN KUPRUM

Oleh

WAN TZE PENG

Mac 2016

Pengerusi: Prof. Madya Abdul Halim Bin Abdullah, PhD

Fakulti: Sains

Peningkatan sisa buangan dalam bidang perindustrian disebabkan oleh perkembangan perindustrian yang pesat semakin menarik perhatian dan minat dalam pembangunan teknologi rawatan air kumbahan di negara ini. Tujuan kajian ini adalah untuk menyediakan fotomangkin yang mudah, tinggi kecekapan dan mesra alam bersertakan eksperimen fotopemangkinan yang ringkas dan boleh ditanggung. Dalam kajian ini, satu siri fotomangkin bismut(III) vanadat ($BiVO_4$) telah disediakan melalui kaedah pemendakan dan satu siri fotomangkin $BiVO_4$ dimuatkan dengan kuprum (Cu-$BiVO_4$) telah disediakan melalui kaedah pengisitepuan.

Analisa XRD menunjukkan bahawa fasa tetragonal $BiVO_4$ telah dibentuk semasa proses pemendakan dan transformasi fasa dari tetragonal ke fasa monoklinik $BiVO_4$ berlaku sepenuhnya pada suhu 450 °C selepas 4 jam pengkalsinan dalam udara. Saiz krystalit fotomangkin yang dihasilkan merangkumi 25.8 – 51.1 nm. $BiVO_4$ yang dihasilkan berbentuk sfera, sebagaimana yang ditunjukkan pada imej FESEM, dengan luas permukaan 0.2 – 0.8 m^2g^{-1}. Saiz zarah fotomangkin diperolehi melalui TEM, adalah dalam lingkungan 34.1 – 60.6 nm. Keputusan dari UV/Vis DRS menunjukkan bahawa tenaga jurang jalur $BiVO_4$ telah ditingkatkan oleh pemuatan kuprum. Kehadiran kuprum dalam fotomangkin Cu-$BiVO_4$ telah diwajarkan dengan keputusan AAS.

Kecekapan $BiVO_4$ dan Cu-$BiVO_4$ sebagai fotomangkin telah dinilai dengan fotopemangkinan pewarna Metilena Biru (MB) di bawah penyinaran cahaya nampak. Keadaan optimum fotopemangkinan adalah berdasarkan parameter. Antara fotomangkin $BiVO_4$ tulen, sampel dikalsina pada suhu 550 °C selama 1 jam menunjukkan aktiviti fotopemangkinan yang tertinggi. Peratusan penyingkiran pewarna MB tertinggi dicapai pada kepekatan awal larutan pewarna sebanyak 10 ppm dan pH awal pada 8, dengan memuatkan 1.0 g $BiVO_4$ dalam eksperimen

fotopemangkinan, di bawah penyinaran cahaya lampu pendarfluor 18W pada suhu bilik.

Kecekapan fotopemangkinan $BiVO_4$ telah dipertingkatkan dengan memuatkan logam kuprum (Cu). Cu-$BiVO_4$ 1% peratusan-berat didapati mempamerkan fotopemangkinan yang paling tinggi. Peratusan penyingkiran pewarna MB pada kepekatan awal larutan sebanyak 10 ppm dan pH awal larutan pada 10, menghampiri 99,57%, apabila 0.8 g Cu-$BiVO_4$ 1% peratusan-berat digunakan dalam eksperimen fotopemangkinan, di bawah penyinaran cahaya lampu pendafluor 18W pada suhu bilik. Fotopemangkinan pewarna MB dalam kajian ini mengikuti kinetik tertib pertama.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere and deepest appreciation to my supervisor, Assoc. Prof. Dr. Abdul Halim Abdullah, for his supervision, invaluable guidance, unfailing help and superb tolerance throughout the course of this work. Also, I would like to thank Prof. Dr. Mohd Zobir Hussein for being my co-supervisor.

Not to forget, I would like to express my deepest gratitude to my beloved family who always believe in me, and endured the hardships with me during this study. Without their unconditional love and endless support, it would not been possible for me to complete this Master of Science course and thesis.

Special thanks to all the science officers and laboratory assistants in Department of Chemistry, Institute of Advanced Technology (ITMA), Institute of Bioscience, UPM for their kindest help, services and advice.

Last but not least, I wish to thank all my lab mates of Lab BASL 103 for their ideas and help during my study. Thank you all.

I certify that a Thesis Examination Committee has met on 01 March 2016 to conduct the final examination of Wan Tze Peng on her thesis entitled "Synthesis, Characterization and Performance of Visible Light Active Copper-Loaded Bismuth Vanadate Photocatalyst" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Nor Azah binti Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Irmawati bt. Ramli, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Chong Fai Kait, PhD
Associate Professor
Fundamental and Applied Sciences Department
Universiti Teknologi Petronas
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 June 2016

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Abdul Halim Bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zobir Bin Hussein, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

____
BUJANG KIM HUAT, PhD
Profesor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- This thesis is my original work;
- Quotations, illustrations and citations have been duly referenced;
- This thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- Intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- Written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- There is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ________________________ Date: ______________________

Name and Matric No.: ____

Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
- Supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ________________________
Name of Chairman of Supervisory Committee: Associate Prof. Dr. Abdul Halim Bin Abdullah

Signature: _________________________
Name of Member of Supervisory Committee: Prof. Dr. Mohd Zobir Bin Hussein

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BET	Brunauer, Emmet, and Teller
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
TGA	Thermogravimetry Analysis
TEM	Transmission Electron Microscopy
AAS	Atomic Absorption Spectroscopy
XRD	X-ray Diffractometry
UV	Ultra-violet
UV/Vis	UV-visible
DRS	Diffuse Reflectance Spectroscopy
C/C_0	relative concentration
AOP	Advanced Oxidation Processes
MB	Methylene Blue
e^-	excited electron
h^+	positive hole
JCPDS	Joint Committee on Powder Diffraction Standards

CHAPTER 1

INTRODUCTION

1.1 Background

Water is the most exquisite part of the Mother Nature which is essential and critical for human and industrial development. Industrial activities have become a huge source of water pollution due to rapid development. It produces pollutants that are extremely harmful to people and the environment. Many industrial facilities use fresh water to carry away the wastes from the plant and into rivers, lakes and oceans. Due to the addition of industrial wastes containing organic pollutants and heavy metals into the river water, the quality of water has become worse. In the last few decades the demand of fresh water rises tremendously due to increasing population and rapid industrialization (Mir et al., 2013; Yisa and Jimoh, 2010).

Malaysia is subsidized with bounty of natural water resources that contributes significantly to the socioeconomic development of the country (Moorthy and Jeyabalan, 2012). Department of Environment in their Environmental Quality Report showed that 46% river water of Malaysia is polluted, which is higher than previous couple of years (DOE, 2011). The production of wastes in the industrial field is the reciprocity to the production of products, which urge the country to bring more concern and interest on the development and utilization of the technologies in wastewater treatment.

Satisfactory disposal of wastewater, whether by surface, subsurface methods or dilution is dependent on its treatment prior to disposal. Appropriate treatment is required to prevent contamination of receiving water to a degree which might interfere with their best or intended use, whether it is for water supply, recreation, industrial use or any other required purpose.

Wastewater treatment applies known technology to improve or upgrade the quality of a wastewater. Normally it involves collecting the wastewater in a central, segregated location (the Wastewater Treatment Plant) and subjecting the wastewater to various treatment processes. Most of the time, since large volume of wastewater is involved, treatment processes are carried out on continuously flowing wastewater (continuous flow or "open" systems) rather than as "batch" or a series of periodic treatment processes in which treatment is carried out on parcels or "batches" of wastewater. While most wastewater treatment processes are continuous flow, certain operations such as vacuum filtration, the addition of chemicals, storage of sludge, filtration and removal or disposal of the treated sludge, are routinely conducted as periodic batch operations.

Wastewater treatment, however, can categorize by the nature of the treatment process used, which are physical, chemical or biological. Physical methods include processes where no gross chemical or biological changes are carried out and strictly physical phenomena are used to treat the wastewater. Examples would be coarse screening to remove larger entrained objects and sedimentation (or clarification). In the process of sedimentation, physical phenomena relating to the settling of solids by gravity are allowed to operate. Normally this consists of simply holding a wastewater for a short period of time in a tank under tranquil conditions, allowing the heavier solids to settle, and removing the "clarified" effluent. Sedimentation for solids separation is a very common process operation and is routinely applied at the beginning and end of wastewater treatment operations. Another common physical treatment processes is aeration, that is, physically adding air to provide oxygen to the wastewater. Filtration is another physical phenomenon used in the treatment where wastewater is passed through a filter medium to separate solids. An example would be the use of sand filters to further remove entrained solids from a treated wastewater. Certain phenomena will occur during the sedimentation process and can be advantageously used to further improve water quality. Permitting greases or oils, for example, to float on the surface and skimming or physically removing them from the wastewater is often carried out as part of the overall treatment process (GO Green Solutions, 2011).

Biological treatment methods use microorganisms, mostly bacteria, in the biochemical decomposition of wastewater to stable end products. More microorganisms or sludge are formed and a portion of the waste is converted to carbon dioxide, water and other end products. Generally, biological treatment methods can be divided into aerobic and anaerobic based on the availability of dissolved oxygen in the wastewater. The purpose of this treatment is basically to remove solids from the wastewater to allow the remainder to be discharged to receiving water without interfering with its best or proper use. The solids which are removed are basically organic but may also include inorganic solids (Muhammad, 2009; Wang et al., 2004).

Chemical treatment methods consist of applying certain chemical reactions or processes to improve the quality of water. The most commonly used chemical process is chlorination where chlorine as a strong oxidizing chemical, is used to kill bacteria and to slow down the rate of decomposition of the wastewater. Bacterial kill is achieved when vital biological processes are affected by the chlorine. Ozone is another strong oxidizing agent that has also been used as an oxidizing disinfectant. Other commonly used chemical process in many industrial wastewater treatment operations is neutralization which acid or base is added to the wastewater to adjust the pH level back to neutral. For instance, lime which is a base is sometimes used in the neutralization of acid waste. Precipitation or coagulation on the other hand, is a process in which an insoluble end product that serves to remove substances from the wastewater is formed by the addition of a chemical, through a chemical reaction. Polyvalent metals are commonly used as precipitating/coagulating chemicals in wastewater treatment. Typical precipitants/coagulants would include lime (that can also be used in neutralization), certain iron containing compounds (such as ferric chloride or ferric sulfate) and alum (aluminum sulfate). Certain processes may actually be physical and chemical in nature. The use of activated carbon to adsorb or remove organic compounds, for example, involves both chemical and physical processes (GO Green Solutions, 2011). Although the mentioned methods above are widely used in the treatment of wastewater, there is still potential on the production of secondary pollutants after the treatments.

Advanced oxidation processes (AOPs) technique is the simple and effective technique which is capable to degrade wide range of organic and non-biodegradable compounds to environmental friendly end products (complete mineralization) has drawn intensive attention in the field. The importance of these processes is due to the high reactivity and redox potential of free radical generated in the process that reacts non-selectively with organic matter present in wastewater. Another advantage of this technique is that the processes can be applied under mild experimental conditions that is, at atmospheric ambient pressure and room temperature.

Photocatalysis is one of the AOP techniques in which the catalytic reaction is induced by the presence of light. In the photocatalysis process, light is absorbed by an adsorbed substrate. The photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (OH•) able to undergo secondary reactions. Its comprehension has been made possible ever since the discovery of water electrolysis by means of the titanium dioxide (TiO_2).

Monoclinic bismuth(III) vanadate ($BiVO_4$) with band gap energy of 2.4 eV has been reported to be an active photocatalyst under visible-light irradiation, therefore attracting considerable attention (Wang et al., 2009; Yu et al., 2006; Zhou et al., 2006). There are three crystalline phases reported for synthetic $BiVO_4$; monoclinic scheelite, tetragonal scheelite and tetragonal zircon. According to previous studies, the monoclinic scheelite phase of $BiVO_4$ shows much higher photocatalytic activity under visible-light irradiation than the other forms (Tokunaga et al., 2001).

Methylene blue (MB) is used as the model dye in this study for evaluation of the photocatalytic efficiency of the synthesized photocatalysts under visible-light irradiation. MB is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}ClN_3S$. It has many uses in a range of different fields, such as biology and chemistry. It appears as a solid, odorless, dark-green powder that yields a blue solution when dissolved in water at room temperature. This dye is stable and incompatible with bases, reducing agents, and strong oxidizing agents. During a chemical or biological reaction pathway, these dye compounds not only deplete the dissolved oxygen in water bodies but also release some toxic compounds to endanger aquatic life (Obata and Koizumi, 1957; Obata et al., 1959). MB is an important cationic dye which is used in many textile manufacturers and it releases aromatic amines (e.g., benzidine, methylene) and is a potential carcinogen (Muhammad et al., 2009). MB has been reported to be photobleached, demethylated, and photodegraded under visible light irradiation on a proper catalyst (Yogi et al., 2008).

1.2 Problem statement

To prevent the production of secondary pollutants (pollutants produced in treatment process), researchers have invented plenty of treatment methods to solve this problem. There is always more than one treatment processes required to treat the wastewater. Although the biological and chemical treatment processes mentioned above can be apply in the secondary stage of treatment to degrade the chemical compounds to the complete mineralization, the simplicity, flexibility, cost of maintenance and duration of the whole processes are the another important concern of the industry.

As of now, advanced oxidation processes (AOP) technique has been proven to be the best alternative method for the treatment of wastewater which fits the industrial requirements. Thus, photocatalysis is one of the main chemical routes for destruction of environmental toxic pollutants. Metal oxide semiconductor photocatalysts are playing an important role in many industrial and technological processes, in both environmental and biomedical application (Sangpour et al., 2010; Martha et al., 2005; Kastner et al., 1999; Hoffmann et al., 1995; Kiwi et al., 1993). In particular, photocatalytic degradation using TiO_2 which is one of the famous metal oxide semiconductor photocatalyst has been extensively studied (Fujishima et al., 2000). However, TiO_2 is only effective under ultra-violet (UV) light. Thus, the development of a visible-light-driven photocatalyst has been a popular concern in this field.

Monoclinic $BiVO_4$ is one of the visible-light-driven photocatalyst which has drawn great interest among the researchers in recent years. However, some reports indicate that the photocatalytic activity of pure $BiVO_4$ is comparatively low. It has been reported that loading metals or metal oxides on the $BiVO_4$ surface could suppress the recombination of photogenerated electrons and holes at the photocatalyst/cocatalyst interfaces (Kohtani et al., 2005). Other studies found that copper was a better dopant in terms of the photocatalytic activity efficiency, in comparison to undoped catalyst (Gao et al., 2011; Jiang et al., 2009; Xu et al., 2008; Huang et al., 2006). Thus, the loading of copper on photocatalysts could be an efficient way to enhance the photocatalytic activity.

In summary, the aim of the wastewater treatment research and development is to overcome the weaknesses and problems encountered by using current treatment processes. This includes omitting the secondary treatment process, in which a simpler and more economical way that is suitable and affordable by all scale of industry can be developed. The goals of this work were to synthesize environment-friendly Cu-loaded $BiVO_4$ photocatalysts and to design easy and economical photodegradation experiments, which can works under low-wattage visible-light irradiation instead of expensive UV light and high efficiency in degrading MB dye.

1.3 Scope of research

The scopes of this research are;

a) To synthesize bismuth vanadate, $BiVO_4$ photocatalysts via precipitation method and Cu-loaded bismuth vanadate, Cu-$BiVO_4$ photocatalysts via impregnation method.
b) To characterize the synthesized bismuth vanadate and Cu-loaded bismuth vanadate photocatalysts.
c) To evaluate and optimize the efficiency of the synthesized bismuth vanadate and Cu-loaded bismuth vanadate photocatalysts in degrading methylene blue (MB) under visible-light irradiation.

REFERENCES

Al-Rasheed, R.A. (2005). Water Treatment By Heterogeneous Photocatalysis An Overview. *Saline Water Desalination Research Institute*

Alekabi, H. and Serpone, N. (1988). Kinetic studies in heterogeneous photocatalysis. 1. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO_2 supported on a glass matrix. *The Journal of Physical Chemistry* 92: 5726-5731.

Amano, F., Nogami, K. and Ohtani, B. (2009). Visible Light-Responsive Bismuth Tungstate Photocatalysts: Effects of Hierarchical Architecture on Photocatalytic Activity. *The Journal of Physical Chemistry* 113: 1536–1542.

Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999). Advanced oxidation processes (AOP) forwater purification and recovery. *Catalysis Today* 53: 51–59.

Bandara, J., Udawatta, C.P.K. and Rajapakse, C.S.K. (2005). Highly stable CuO incorporated TiO_2 catalyst for photocatalytic hydrogen production from H_2O. *Photochemical & Photobiological Sciences* 4: 857-861.

Behnajady, M.A., Modirshahla, N., Shokri, M. and Rad, B. (2008). Enhancement of photocatalytic activity of TiO_2 nanoparticles by silver doping: photodeposition versus liquid impregnation methods. *Global NEST Journal* 10: 1-7.

Bhatkhande, D.S., Pangarkar, V.G. and Beenackers, A.A.C.M. (2001). Photocatalytic Degradation for Environmental Applications—a Review. *Journal of Chemical Technology* and *Biotechnology* 77: 102–116.

Bhattacharya, A.K., Mallick, K.K. and Hartridge, A. (1997). Phase transition in $BiVO_4$. *Materials Letters* 30: 7-13.

Campanati, M., Fornasari, G. and Vaccari, A. (2003). Fundamentals in the preparation of heterogeneous catalysts. *Catalysis Today* 77: 299.

Chakrabarti, S. and Dutta, B.K. (2004). Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *Journal of* Hazardous *Materials* 112: 269-278.

Chatchai, P., Murakami, Y., Kishioka, S., Nosaka, A.Y. and Nosaka, Y. (2009). Efficient photocatalytic activity of water oxidation over $WO_3/BiVO_4$

composite under visible light irradiation. *Electrochimica Acta* 54: 1147–1152.

Chiang, K., Amal, R. and Tran, T. (2002). Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide. *Journal of Advances in Environmental Research* 6: 471–485.

Choi, W.Y., Termin, A. and Hoffmann, M.R. (1994). Role of Metal Ion Dopants in Quantum Sized TiO_2 Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *The Journal of Physical Chemistry* 98: 13669-13679.

Devipriya, S. and Yesodharan, S. (2005). Photocatalytic degradation of pesticide. Contaminants in water. *Solar Energy Materials and Solar Cells* 86:309-348.

Ding, Z., Martens, W. and Frost, R.L. (2002). Thermal activation of copper nitrate. *Journal of Materials Science Letters* 21: 1415-1417.

DOE, *Environmental Quality Report 2009: River Water Quality.* Department of Environment. Ministry of Natural Resources and Environment: Putrajaya. 2011.

Dorfman, L. M. and Adams, G. E. (1973). National Standard Reference Data System, *National Bureau of Standards* 46: 1-59.

Dunkle, S.S., Helmich, R.J. and Suslick, K.S. (2009). $BiVO_4$ as a Visible-Light Photocatalyst Prepared by Ultrasonic Spray Pyrolysis. *The Journal of Physical Chemistry C* 113: 11980–11983.

Evgenidou, E., Fytianos, K. and Poulios, I. (2005). Photocatalytic oxidation of dimethoate in aqueous solutions. *Journal of Photochemistry and Photobiology A: Chemistry* 175:29–38.

Fernandes, F.M., Araújo, R., Proença, M.F., Silva, C.J.R. and Paiva, M.C. (2007). Functionalization of carbon nanofibers by a Diels-Alder addition reaction. *Journal of Nanoscience and Nanotechnology* 7: 3514.

Frietsch, M., Zudock, F., Goschnick, J. and Bruns, M. (2000). CuO catalytic membrane as selectivity trimmer for metal oxide gas sensors. *Sensors and Actuators B: Chemical* 65: 379-381.

Fujishima, A. and Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 238: 37-38.

Fujishima, A., Hashimoto, K. and Watanabe, T. (1999). TiO_2 photocatalysis:fundamentals and applications. *BKC, Tokyo*

Fujishima, A., Rao, T.N. and Tryk, D.A. (2000). Titanium dioxide photocatalysis. Journal of *Photochemistry* and *Photobiology C*: *Photochemistry Reviews* 1: 1-21.

Gao, X.M., Wu, Y.F., Wang. J., Fu, F., Zhang, L.P. and Niu, F.X. (2011). The Preparation of Cu-$BiVO_4$ and its Enhanced Photocatalytic Properties for Degradation of Phenol. *Advanced Materials Research*, 356-360: 1253-1257.

Gaya, U.I. (2011). Comparative analysis of ZnO-catalyzed photo-oxidation of *p*-chlorophenols. *European Journal of Chemistry* 2: 163-167.

Ge, L. (2008). Novel Pd/$BiVO_4$ composite photocatalysts for efficient degradation of methyl orange under visible light irradiation. *Materials Chemistry and Physics* 107: 465-470.

Ghijsen, J., Tjeng, L.H., Elp, J., Eskes, H., Westerink, J., Sawatzky, G.A., Czyzyk, M.T. (1988). Electronic structure of Cu_2O and CuO. *Physical Review B: Condensed Matter* 38: 11322-11330.

Glaze, W.H., Kang, J.W. and Chapin, D.H. (1987). The chemistry of water treatment involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Science & Engineering* 9: 335-342.

GO Green Solutions, Wastewater Treatment Methods, 2011, http://www.gogreensolu.com/index.php?option=com_content&view=article&id=64:wastewater-treatment-methods-&catid=1:latest-news (accessed 30 Sep. 2015)

Gotic, M., Music, S., Ivanda, M., Soufek, M. and Popovic, S. (2005). Synthesis and characterisation of bismuth(III) vanadate. *Journal of Molecular Structure* 744: 535-540.

Gouvea, C.A.K., Wypych, F., Moraes, S.G., Duran, N., Nagata, N. and Peralta, Z.P. (2000). Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution. *Chemosphere* 40: 433.

Grela, M.A. and Colussi, A.J. (1996). Kinetics of Stochastic Charge Transfer and Recombination Events in Semiconductor Colloids. Relevance to Photocatalysis Efficiency. *The Journal of Physical Chemistry* 100: 18214–18221.

He, C. and Gu, M. (2006). Photocatalytic activity of bismuth germanate $Bi_{12}GeO_{20}$ powders. *Scripta Materialia* 54: 1221–1225.

Hindeleh, A.M. and Johnson, D.J. (1978). Crystallinity and crystallite size measurement in polyamide and polyester fibres. *Polymer* 19: 27-32.

Hoffmann, M.R., Martin, S.T., Choi W.Y. and Bahnemann, D.W. (1995). Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews* 95: 69-96.

Huang, J., Wang, S., Zhao, Y., Wang, X., Wang, S., Wu, S., Zhang, S. and Huang, W. (2006). Synthesis and characterization of CuO/TiO_2 catalysts for low-temperature CO oxidation. *Catalysis Communications* 7: 1029–1034.

Jayalakshmi, M. and Balasubramanian, K. (2009). Hydrothermal Synthesis of $CuO-SnO_2$ and $CuO-SnO_2-Fe_2O_3$ Mixed Oxides and their Electrochemical Characterization in Neutral Electrolyte. *International Journal of Electrochemical Science* 4: 571-581.

Jiang, H, Endo, H., Natori, H., Nagai, M. and Kobayashi, K. (2009). Fabrication and efficient photocatalytic degradation of methylene blue over $CuO/BiVO_4$ composite under visible-light irradiation. *Materials Research Bulletin* 44: 700–706.

Jung, M., Lee, J., Park, S., Kim, H. and Chang, J. (2005). Investigation of the annealing effects on the structural and optical properties of sputtered ZnO thin films. *Journal of Crystal Growth* 283: 384–389.

Kako, T., Kikugawa, N. and Ye, J. (2008). Photocatalytic activities of $AgSbO_3$ under visible light irradiation. *Journal of Catalysis Today* 131: 197-202.

Kastner, J.R., Thompson, D.N. and Cherry Kaster, R.S. (1999). Photoenhanced Degradation of Methylene Blue on Cosputtered $M:TiO_2$ (M = Au, Ag, Cu) Nanocomposite Systems: A Comparative Study. *Enzyme* and *Microbial Technology* 24: 104.

Kansal, S.K., Singh, M. and Sud, D. (2008). Studies on TiO_2/ZnO photocatalysed degradation of lignin. *Journal of Hazardous Materials* 153: 412-417.

Ke, D., Peng, T., Ma, L., Cai, P. and Dai, K. (2009). Effects of hydrothermal temperature on the microstructures of $BiVO_4$ and its photocatalytic O_2 evolution activity under visible light. *Inorganic Chemistry* 48: 4685–4691.

Kiwi, J., Pulgarin, C., Peringer, P. and Gratzel, M. (1993). Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in wastewater treatment. *Applied Catalysis B*: *Environmental* 3: 85-99.

Kohtani, S., Koshiko, M., Kudo, A., Tokumura, K., Ishi-gaki, Y., Toriba, A., Hayakawa, K. and Nakagaki, R. (2003). Photodegradation of 4-alkylphenols using $BiVO_4$ photocatalyst under irradiation with visible light from a solar simulator. *Applied Catalysis B* 46: 573–586.

Kohtani, S., Hiro, J., Yamamoto, N., Kudo, A., Tokumura, K. and Nakagaki, R. (2005). Adsorptive and Photocatalytic Properties of Ag-Loaded $BiVO_4$ on the Degradation of 4-Nalkylphenols under Visible Light Irradiation. *Catalysis Communications* 6: 185-189.

Kohtani, S., Tomohiro, M., Tokumura, K. and Nakagaki, R. (2005). Photooxidation reactions of polycyclic aromatic hydrocarbons over pure and Ag-loaded $BiVO_4$ photocatalysts. *Applied Catalysis B*: *Environmental* 58: 265–272.

Kommineni, S., Zoeckler, J., Stocking, A.J., Liang, S., Flores, A.E. and Kavanaugh, M.C. 3.0 Advanced Oxidation Processes. In *Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water: Air Stripping, Advanced Oxidation Process, Granular Activated Carbon, Synthetic Resin Sorbents*. California MTBE Research Partnership. National Water Research Institute: California. 2000.

Konstantinou, I.K. and Albanis, T.A. (2004). TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations a review. *Applied Catalysis B: Environmental* 49: 1–14.

Kosowska, S.K., Hoellman, D.B., Lin, G., Clark, C., Credito, K., McGhee, P., Dewasse, B., Bozdogan, B., Shapiro, S. and Appelbaum, P.C. (2005). Anti pneumococcal activity of ceftobiprole, a novel broad-spectrum cephalosporin. *Antimicrob Agents Chemother* 49: 1932–1942.

Kudo, A., Omori, K. and Kato, H. (1999). A novel aqueous process for preparation of crystal form-controlled and highly crystalline $BiVO_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. *Journal of the American Chemical* Society 121: 11459–11467.

Kudo, A., Tsuji, I. and Kato, H. (2002). $AgInZn_7S_9$ solid solution photocatalyst for H_2 evolution from aqueous solutions under visible light irradiation. *Chemical Communications* 17: 1958-1959.

Legrini, O., Oliveros, E. and Braun, A. M. (1993). Photochemical processes for water treatment. *Chemical Reviews* 93: 671-698.

Li, H., Liu, G. and Duan, X. (2009). Monoclinic $BiVO_4$ with regular morphologies: hydrothermal synthesis, characterization and photocatalytic properties. *Materials Chemistry and Physics* 115: 9–13.

Liu, J., Wang, H., Wang, S. and Yan, H. (2003). Hydrothermal preparation of $BiVO_4$ powders. *Materials Science and Engineering: B* 104: 36–39.

Liu, W., Cao, L., Su, G., Liu, H., Wang, X. and Zhang, L. (2010). Ultrasound assisted synthesis of monoclinic structured spindle $BiVO_4$ particles with hollow structure and its photocatalytic property. *Ultrasonics Sonochemistry* 17: 669–674.

Liu, Y., Huang, B., Dai, Y., Zhang, X., Qin, X., Jiang, M. and Whangbo, M.H. (2009). Selective Ethanol Formation from Photocatalytic Reduction of Carbon Dioxide in Water with $BiVO_4$ Photocatalyst. *Catalysis Communications* 11: 210-213.

Long, M.C., Cai, W.M., Cai, J., Zhou, B.X., Chai, X.Y. and Wu, Y.H. (2006). Efficient photocatalytic degradation of phenol over Co_3O_4/$BiVO_4$ composite under visible light irradiation. *The Journal of Physical Chemistry B* 110: 20211–20216.

Martha Miller, J. and Grant Allen, D.J. (2005). Modelling transport and degradation of hydrophobic pollutants in biofilter biofilms. *Chemical Engineering Journal* 113: 197-204.

Martin, T.Z., Orton, G.S., Travis, L.D., Tamppari, L.K. and Claypool, I. (1995). Observation of Shoemaker-Levy impacts by the Galileo Photopolarimeter Radiometer. *Science* 268: 1875-1879.

Martirosyan, K. A. (1972). On the Reggeon graph scheme at available, not ultra-high, energies. *Nuclear Physics B* 36: 566–574.

Mills, A., Davies, R.H. and Worsley, D. (1993). Water purification by semiconductor photocatalysis. *Chemical Society Reviews* 22: 417-426.

Mills, A. and Morris, S. (1993). Photomineralization of 4-chlorophenol Sensitized by Titanium Dioxide: A Study of the Initial Kinetics of Carbon Dioxide Photogeneration. *Journal of Photochemistry and Photobiology A: Chemistry* 71: 75-83.

Mir, S.I., Hossain, M.A., Nasly, M.A. and Sobahan, M.A. (2013). Effect of Industrial Pollution on the Spatial Variation of Surface Water Quality. *American Journal of Environmental Sciences* 9: 120-129.

Monshi, A., Foroughi, M.R. and Monshi, M.R. (2012). Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD. *World Journal of Nano Science and Engineering* 2: 154-160.

Moorthy, R. and Jeyabalan, T. (2012). Ethics and sustainability: A review of water policy and management. *American Journal of Applied Sciences* 9: 24-31.

Moura, A.P., Cavalcante, L.S., Sczancoski, J.C., Stroppa, D.G., Paris, E.C., Ramirez, A.J., Varela, J.A. and Longo, E. (2010). Structure and growth mechanism of CuO plates obtained by microwave-hydrothermal without surfactants. *Advanced Powder Technology* 21: 197–202.

Muggli, D.L., Lecourt, M. and Harrison, P.J. (1996). Effects of iron and nitrogen source on the sinking rate, physiology and metal composition of an oceanic diatom from the subarctic Pacific. *Marine Ecology Progress Series* 132: 215-227.

Muhammad, A, Rauf, I, Shehadeh, A. Amal, A. and Al-Zamly. (2009). Removal of Methylene Blue from Aqueous Solution by Using Gypsum as a Low Cost Adsorbent. *World Academy of Science, Engineering and Technology* 31: 609–613.

Muhammad Irfan. (2009). Wastewater Treatment in Textile, Tanneries and Electroplating Industries especially by Activated Sludge Method- A technical report. *Journal of Pakistan Institute of Chemical Engineers* 37: 35-50.

Obata, H. and Koizumi, M. (1957). Photochemical Reactions between Methylene Blue and Tri, Di and Monomethylamine. II. *Bulletin of The Chemical Society of Japan* 30: 142.

Obata, H., Kogasaka and K., Koisumi, M. (1959). Photochemical reactions between methylene blue and tri-, di-, and monomethylamine. III. Behavior of methylene blue in the presence of oxygen. *Bulletin of the Chemical Society of Japan* 32: 125.

Ohko, Y., Tryk, D.A., Hashimoto, K. and Fujishima, A. (1998). Autoxidation of acetaldehyde initiated by TiO_2 photocatalysis under weak UV illumination. *The Journal of Physical Chemistry B* 102: 2699–2704.

Pardeshi, S.K., and Patil, A.B. (2008). A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy. *Solar Energy, 82*: 700-705.

Pardeshi, S.K. and Patil, A.B. (2009). Solar photocatalytic degradation of resorcinol a model endocrine disrupter in water using zinc oxide. *Journal of Hazardous Materials* 163: 403–409.

Parvaneh Sangpour, Fatemeh Hashemi, and Alireza Z. Moshfegh. (2010). Photoenhanced Degradation of Methylene Blue on Cosputtered M:TiO_2 (M = Au, Ag, Cu) Nanocomposite Systems: A Comparative Study. *The Journal of Physical Chemistry C* 114: 13955-13961.

Pookmanee, P., Kojinok, S. and Phanichphant, S. (2012). Bismuth Vanadate ($BiVO_4$) Powder Prepared by the Sol-gel Method. *Journal of Metals, Materials and Minerals* 22: 49-53.

Rivera-Utrilla, J., Bautista-Toledo, I., Ferro-Garcı´a, M. and Moreno-Castilla, C. (2001). Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *Journal of Chemical Technology* and *Biotechnology* 76: 1209.

Rullens, F., Laschewsky, A. and Devillers, M. (2006). Bulk and thin films of bismuth vanadates prepared from hybrid materials made from an organic polymer and inorganic salts. *Chemistry of Materials* 18: 771-777.

Sayama, K., Nomura, A., Arai, T., Sugita, T., Abe, R., Yanagida, M., Oi, T., Iwasaki, Y., Abe, Y. and Sugihara, H. (2006). Photoelectrochemical decomposition of water into H_2 and O_2 on porous $BiVO_4$ thin-film electrodes under visible light and significant effect of Ag ion treatment. *Journal of Physical Chemistry B* 110: 11352–11360.

Serpone, N. and Emeline, A.V. (2002). Suggested Terms and Definitions in Photocatalysis and Radiocatalysis. *International Journal of Photoenergy* 4: 91-131.

Shang, M., Wang, W., Sun, S., Ren, J., Zhou, L. and Zhang, L. (2009). Efficient visible light-induced photocatalytic degradation of contaminant by spindle-like PANI/$BiVO_4$. *Journal of Physical Chemistry C* 113: 20228–20233.

Shen, Y., Huang, M.L., Huang, Y., Lin, J.M. and Wu, J.H. (2010). The synthesis of bismuth vanadate powders and their photocatalytic properties under visible light irradiation. *Journal of Alloys and Compounds* 496: 287–292.

Slamet, Nasution, H.W., Purnama, E., Kosela, S. and Gunlazuardi, J. (2005). Photocatalytic reduction of CO_2 on copper-doped Titania catalysts prepared by improved-impregnation method. *Catalysis Communications* 6: 313-319.

Sleight, A.W., Chen, H.Y., Ferretti, A. and Cox, D.E. (1979). Crystal growth and structure of $BiVO_4$. *Materials Research Bulletin* 14: 1571-81.

Smith, H.M. (2002). High Performance Pigments. *Weinheim: Wiley-VCH.*

Stylidi, M., Kondarides, D.I. and Verykios, X.E. (2004). Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO_2 suspensions. *Applied Catalysis B: Environmental* 47: 189–201

Tang, X.F., Li, Y.G., Huang, X.M., Xu, Y.D., Zhu, H.Q., Wang, J.G. and Shen, W.J. (2006). MnOx-CeO2 mixed oxide catalysts for complete oxidation of formaldehyde: Effect of preparation method and calcination temperature. *Applied Catalysis B*: *Environmental* 62: 265.

Tauc, J. and Menth, A.J. (1972). States in the gap. *Journal of Non-Crystalline Solids* 8-10: 569-585.

Tokunaga, S., Kato, H. and Kudo, A. (2001). Selective Preparation of Monoclinic and Tetragonal $BiVO_4$ with Scheelite Structure and Their Photocatalytic Properties. *Chemistry of Materials* 13: 4624–4628.

Tomašić, V. and Jović, F. (2006). State of the art in the monolithic catalysts/reactors. *Applied Catalysis A: General* 311: 112-21.

Trikalitis, P.N., Rangan, K.K., Bakas, T. and Kanatzidis, M.G. (2001). Varied pore organization in mesostructured semiconductors based on the $[SnSc_4]^{(4-)}$ anion. *Nature* 410: 671–675.

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

Tseng, T.K., Lin, Y.S., Chen, Y.J. and Chu, H. (2010). A Review of Photocatalysts Prepared by Sol-Gel Method for VOCs Removal. *International Journal of Molecular Sciences* 11: 2336–2361.

Wang, C., Zhao, J.C., Wang, X.M., Mai, B.X., Sheng, G.Y., Peng, P.A. and Fu, J.M. (2002). Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO_2 coupled photocatalysts. *Applied Catalysis B*: *Environmental* 39: 269–279.

Wang, F., Shao, M., Cheng, L., Hua, J. and Wei, X. (2009). The synthesis of monoclinic bismuth vanadate nanoribbons and studies of photoconductive, photoresponse, and photocatalytic properties. *Materials Research Bulletin* 44: 1687-1691.

Wang, L.K., Hung, Y.T., Lo, H.H. and Yapijakis, C. (2004). *Handbook of Industrial and Hazardous Wastes Treatment (2nd edition).* New York: Marcel Dekker, Inc.

Wu, D.F., Jiang, W. and Zhou, J.C. (2010). Effect of drying and calcination on the toluene combustion activity of a monolithic CuMnAg/Γ-Al_2O_3/cordierite catalyst. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)* 85: 569–576.

Xu, H., Li, H., Wu, C., Chu, J., Yan, Y. and Shu, H. (2008). Preparation, characterization and photocatalytic activity of transition metal-loaded $BiVO_4$. *Materials Science and Engineering: B* 147: 52–56.

Xu, H., Li, H., Wu, C., Chu, J., Yan, Y., Shu, H. and Gu, Z. (2008). Preparation, characterization and photocatalytic properties of Cu-loaded $BiVO_4$. *Journal of Hazardous Materials* 153: 877–884.

Yamaguchi, O., Mukaida, Y., Shigeta, H., Takemura, H. and Yamashita, M. (1988). Preparation of Alkoxy-Derived Yttrium Vanadate. *Journal of the Electrochemical Society* 136: 1557-1560.

Yang, T. and Xia, D. (2009). Self-assembly of highly crystalline spherical $BiVO_4$ in aqueous solutions. *Journal of Crystal Growth* 311: 4505–4509.

Yao, W.F., Wang, H., Xu, X.H., Shang, S.X., Hou, Y., Zhang, Y. and Wang, M. (2003). Synthesis and photocatalytic property of bismuth titanate $Bi_4Ti_3O_{12}$. *Materials Letters* 57: 1899-1902.

Yin, W., Wang, W., Shang, M., Zhou, L., Sun, S. and Wang, L. (2009). $BiVO_4$ hollow nanospheres: anchoring synthesis, growth mechanism, and their application in photocatalysis. *European Journal of Inorganic Chemistry* 2009: 4379–4384.

Yin, Y., Walsh, A.G., Vamivakas, A.N., Cronin, S.B., Prober, D.E. and Goldberg, B.B. (2011). Electron-phonon coupling of G mode and assignment of a combination mode in carbon nanotubes. *Physical Review B* 84: 075428.

Yisa, J. and Jimoh, T. (2010). Analytical Studies on Water Quality Index of River Landzu. *American Journal of Applied Sciences* 7: 453-458.

Yogi, C., Kojima, K., Wada, N., Tokumoto, H., Takai, T., Mizoguchi, T. and Tamiaki, H. (2008). Photocatalytic degradation of methylene blue by TiO_2 film and Au particles-TiO_2 composite film. *Thin Solid Films* 516: 5881-5884.

Yu, J. and Kudo, A. (2005). Hydrothermal synthesis and photocatalytic property of 2-dimensional bismuth molybdate nanoplates. *Chemistry Letters* 34: 1528-1529.

Yu, J. and Kudo, A. (2006). Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized $BiVO_4$. *Advanced Functional Materials* 16: 2163-2169.

Yu, J.G., Yu, J.C., Cheng, B., Hark, S.K. and Iu, K. (2003). The effect of F^--doping and temperature on the structural and textural evolution of mesoporous TiO_2 powders. *Solid State Chemistry* 174: 372–380.

Yu, J., Zhang, Y. and Kudo, A. (2009). Synthesis and photocatalytic performances of BiVO4 by ammonia co-precipitation process. *Journal of Solid State Chemistry* 182: 223–228.

Zhang, A. and Zhang, J. (2009). Characterization of visible-light-driven $BiVO_4$ photocatalysts synthesized via a surfactant-assisted hydrothermal method. *Spectrochimica Acta Part A* 73: 336-341.

Zhang, A., Zhang, J., Cui, N., Tie, X., An, Y. and Li L. (2009). Effects of pH on hydrothermal synthesis and characterization of visible-light-driven $BiVO_4$ photocatalyst. *Journal of Molecular Catalysis A: Chemical* 304: 28–32.

Zhang, L., Chen, D.R. and Jiao, X.L. (2006). Monoclinic structured $BiVO_4$ nanosheets: hydrothermal preparation, formation mechanism, and coloristic and photocatalytic properties. *The Journal of Physical Chemistry B* 110: 2668–2673.

Zhang, H.M., Liu, J.B., Wang, H., Zhang, W.X. and Yan, H. (2008). Rapid microwave-assisted synthesis of phase controlled $BiVO_4$ nanocrystals and research on photocatalytic properties under visible light irradiation. *Journal of Nanoparticle Research* 10: 767–774.

Zhang, X., Ai, Z., Jia, F., Zhang, L., Fan, X. and Zhou, Z. (2007) Selective synthesis and visible light photocatalytic activities of $BiVO_4$ with different crystalline phases. *Materials Chemistry and Physics* 103: 162-167.

Zhao, X., Qu, J.H., Liu, H.J. and Hu, C. (2007). Photoelectrocatalytic degradation of triazine-containing azo dyes at gamma-Bi_2MoO_6 film electrode under visible light irradiation lambda>420 nm. *Journal of Environmental Science and Technology* 41: 6802–6807.

Zhou, L., Wang, W., Liu, S., Zhang, L., Xu, H. and Zhu, W. (2006). A sonochemical route to visible-light-driven high-activity $BiVO_4$ photocatalyst. *Journal of Molecular Catalysis A: Chemical* 252: 120-124.

Zhou, L., Wang, W. and Xu, H. (2008). Controllable Synthesis of Three-Dimensional Well-Defined $BiVO_4$ Mesocrystals via a Facile Additive-Free Aqueous Strategy. *Crystal Growth & Design* 8: 728–733.

Zhou, L., Wang, W., Zhang, L., Xu, H. and Zhu W. (2007). Single-crystalline $BiVO_4$ microtubes with square-cross sections: Microstructure, growth mechanism and photocatalytic property. *Journal of Physic and Chemistry* 111: 13659–13664.

Zhou, Y., Vuille, K., Heel, A., Probst, B., Kontic, R. and Patzke, G.R. (2010). An inorganic hydrothermal route to photocatalytically active bismuth vanadate *Applied Catalysis A: General* 375: 140–148.