UNIVERSITI PUTRA MALAYSIA

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

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By

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

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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

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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

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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.

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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:

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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.

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