

**REMOVAL OF POLLUTANTS USING
NANOSTRUCTURED TUNGSTEN OXIDE**

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**REMOVAL OF POLLUTANTS USING NANOSTRUCTURED TUNGSTEN
OXIDE**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Removal of Pollutants using Nanostructured Tungsten Oxide'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

| | |
|-----------------|---------------------------|
| ° | Degree |
| °C | Degree Celsius |
| °C/min | Degree Celsius per Minute |
| at% | Atomic percent |
| wt% | Weight percent |
| ppm | Part per million |
| W | Tungsten |
| WO ₃ | Tungsten Oxide |
| KOH | Potassium Hydroxide |
| MO | Methyl Orange |
| mg | Milligram |

LIST OF ABBREVIATIONS

| | |
|--------|---|
| AOP | Advanced Oxidation Process |
| CB | Conduction Band |
| VB | Valence Band |
| FESEM | Field Emission Scanning Electron Microscopy |
| EDX | Energy-Dispersive X-ray |
| XRD | X-Ray Diffraction Analysis |
| UV-vis | Ultraviolet-Visible Spectrometry |

REMOVAL OF POLLUTANTS USING NANOSTRUCTURED TUNGSTEN OXIDE

ABSTRAK

Tungsten (W) ialah unsur peralihan logam yang popular dan oksidanya (WO_x) boleh didapati dalam aplikasi dalam bidang elektrik dan elektronik, salutan, serta produk kosmetik. Dalam beberapa tahun ini, tungsten oksida berstruktur nano telah mendapat banyak perhatian kerana sifat dan aplikasinya yang menarik. Di antara pelbagai aplikasi yang ada, foto-pemangkin adalah yang paling menarik dalam degradasi bahan pencemar organik. Bahan nano foto-pemangkin seperti semikonduktor tungsten oksida berstruktur nano (WO_3) boleh menyerap molekul pewarna (sebagai contoh pencemar organik) kemudian mendegredasikan pewarna kepada produk yang kurang berbahaya di bawah sinaran ultraungu (UV). Dengan itu, objektif kerja ini adalah untuk mensintesis WO_3 berstruktur nano dengan menggunakan kaedah pengoksidaan terma kemudian kebolehan penyingkiran pewarna oren (MO) menggunakan WO_3 berstruktur nano yang telah disintesis. Dalam penyelidikan ini, terdapat dua kaedah pengoksidaan terma secara satu-langkah and dua-langkah telah dikaji. Beberapa parameter telah dimanipulasi untuk mengetahui keadaan optimum untuk mensintesis WO_3 berstruktur nano, iaitu kesan tempoh masa penggunaan pemangkin KOH, kesan suhu pengoksidaan terma, kesan kepekatan pemangkin KOH dan kesan kekasaran permukaan tungsten. Teknik pencirian yang digunakan untuk memeriksa sampel yang disintesis termasuk FESEM, XRD dan EDX. Daripada keputusan yang diperolehi, WO_3 berstruktur nano dengan wayar nano berjaya disintesis pada 600 °C dalam keadaan udara biasa tanpa penggunaan KOH sebagai pemangkin. Kecekapan degradasi sampel ini telah mencapai degradasi tertinggi pada 85%.

REMOVAL OF POLLUTANTS USING NANOSTRUCTURED TUNGSTEN OXIDE

ABSTRACT

Tungsten (W) is a popular metallic transition element and its oxide (WO_x) can be found in applications in the field of electrical and electronics, coatings, as well as cosmetic products. In recent years, nanostructured Tungsten Oxide (WO_3) has gained particular attention due to its promising properties and applications. Among all the applications, one of those is as a photocatalyst in the degradation of organic pollutants. The objective of this present work is to synthesis nanostructured WO_3 by using thermal oxidation method and to also investigate the possibility of MO removal using the synthesized nanostructured WO_3 . In this research, two methods were studied, which are one-step and two-step thermal oxidation. Several parameters were manipulated to find out the most optimum to synthesize nanostructured WO_3 , includes the effect of KOH mist flowing time, the effect of thermal oxidation temperatures, the effect of KOH concentration and the effect of surface roughness of the tungsten foil. The characterization techniques used to examine the synthesized samples include FESEM, XRD and EDX. From the result obtained, the nanostructured WO_3 with nanowires was successfully synthesized at 600°C in normal air condition without the presence of KOH acts as catalyst. The degradation efficiency of this sample has achieved the highest degradation (85%).

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the overview of this research and significance of nanostructured tungsten oxide, WO_3 in the removal of organic pollutants. In general, this chapter summarizes the research background of dyes as organic pollutants and the photocatalytic reaction of semiconductor photocatalyst for the removal of dye, the problem statement and the objectives of this final year project.

1.1 Introduction to Dyes

Every day, a large variety industrial operation has been discharging a tremendous amount of chemicals that are hazardous to human health, including those that can cause cancer and cell degeneration. Some of them are able to persist in the environment for an extended period of time in the form of pollutants. Dyes, such as textile dye in wastewater has always been a problem that could not be resolved effortlessly. Dye is colouring materials that often used in the textile industry to colour materials for clothes, home furnishing, and other textiles. Dyes can come in variety of colour and shades. Their characteristic depends on the chemical composition and nature. The most typical dye is the water-soluble anhydrous, or oil-soluble class.

The textile industry has been using array of chemicals for different purposes especially for coloring, so there has been a lot of waste generated from this particular industry. The dye used in textiles is a form of environmental contaminant that degrades very slowly in the natural environment. (Hepel and Luo, 2001). Some dyes may induce cancer and mutations in humans since they are carcinogenic and mutagenic (Joseph and Mathew, 2015) Therefore, total removal of the organic dyes in the wastewater is consequently of the utmost importance.

There have also been some latest innovations in dyeing technologies that are more sustainable and environmentally friendly. In recent years, researchers have been looking for ways to make textile dyes eco-friendly and biodegradable. A variety of measures or approaches have been explored in order to eliminate the dyes pollutant in wastewater as much as possible. Several approaches, for examples heterogenous photocatalysis, ion exchange, microbes, membrane filtration and adsorption, are utilised in an effort to reduce dyes entering waterbodies (Chen and Mao, 2007). Among these approaches, heterogeneous photocatalysis utilising semiconductors metal oxides are seen to be the most interesting. The benefits of photocatalysis approach over conventional ones include the ability to eliminate contaminants in the ppb range, absence of polycyclic compound production and lower cost (Muhd Julkapli et al., 2014). It allows for energy efficiency because it uses sunlight to activate the process.

There are many semiconductor metal oxides or also known as semiconductor photocatalysts that have been demonstrating remarkable dye degradation performances under solar simulated conditions or ultraviolet (UV) light irradiation during the wastewater treatment. Examples of the oxide semiconductors are TiO_2 , ZnO and WO_3 (Saggiaro et al., 2016). Among these semiconductor materials, tungsten oxide (WO_3), is a promising n-type semiconductor material with a band gap energy of 2.8eV. Since the oxide has rather narrow band gap, it is possible to active the photocatalyst using sunlight. Moreover, WO_3 has stable physicochemical properties (Zhao et al, 2014).

1.2 Sources of Dyes Wastes and its Impacts

As reported by the United States “Colour Index”, more than 60000 tons of dyes waste were discharged into the environment worldwide annually. This is due to all those dye waste was left untreated and being discharged illegally, further leads to contamination to the environment. One of main sources of dyes waste is from wastewater treatment plant.

Dyes contain water-soluble materials that do not dissolve completely can be discharged into wastewater during washing or rinsing processes and during dyeing processes. They can also be discharged during rainstorms if wastewater treatment plants are not equipped with adequate infrastructure to handle them or if they overflow into rivers and streams through storm drains. As this goes on, the ecosystem and habitat of the surrounding will be negatively impacted.

Another source of dye waste came from textile industry. The textile industry has a global presence and is responsible for around 1 trillion dollars in revenue, 7% of the entire value of global exports, and the employment of approximately 35 million people in various countries (Desore and Narula, 2018). The unwanted dyes from textile industry are one of the most common pollutants found in water as they get discharged into water as a result of industrial manufacturing and use of fabrics. Once the textile dyes were discharged illegally to enter underground water, they can lead to toxic or poisonous environments that have the potential to adversely affect human health or cause fatal diseases. There is a need for removal techniques that degrade or remove dyes from water before it reaches drinking water sources so that pure water can be obtained for human consumption (Doheny et al., 2011).

The dyes are soluble organic molecules (Mahapatra, 2016), particularly those that fall into the categories of being reactive, direct, basic, or acidic. They have a high level of solubility in water, which makes it challenging to eliminate them using typical traditional methods. (Hassan and Carr, 2018). Because it has chromophoric groups in its molecular structures, it has the ability to give a certain substrate a colour of its own (Shamey and Zhao, 2014) This is one of its characteristics. However, the property of fixing the colour to the material is associated with auxotrophic groups, which are polar and are able to bind to polar groups of textile fibre (Wardman, 2017).

The colour that is linked with textile dyes not only causes aesthetic damage to the water bodies, but it also limits the passage of light through water, which leads to a drop in the rate of photosynthesis and dissolved oxygen levels, which affects the entirety of the aquatic biota (Hassan and Carr, 2018). Besides, the dyes are toxic, mutagenic, and carcinogenic (Khatri et al., 2018), They commonly persist as environmental pollutants and capable of travelling throughout entire food chains; and they provide biomagnification, meaning that organisms that are higher up the food chain show higher levels of contamination compared to their prey (Newman, 2015).

The majority of the organic materials in synthetic dye wastewater are complex and difficult to decompose naturally. Anionic azo dyes make up half of the synthetic dye production. Methyl Orange (MO), also known as dimethylaminoazobenzenesulfonate is a common and typical azo anionic dye. It is a water-soluble organic synthetic dye and has very high colourability as it presents a bright orange colour when dissolved in water. MO molecules are highly toxic and carcinogenic as they contain aromatic and $-N=N-$ groups in their molecules as shown in Figure 1.1 below (Wu, L et al., 2021).

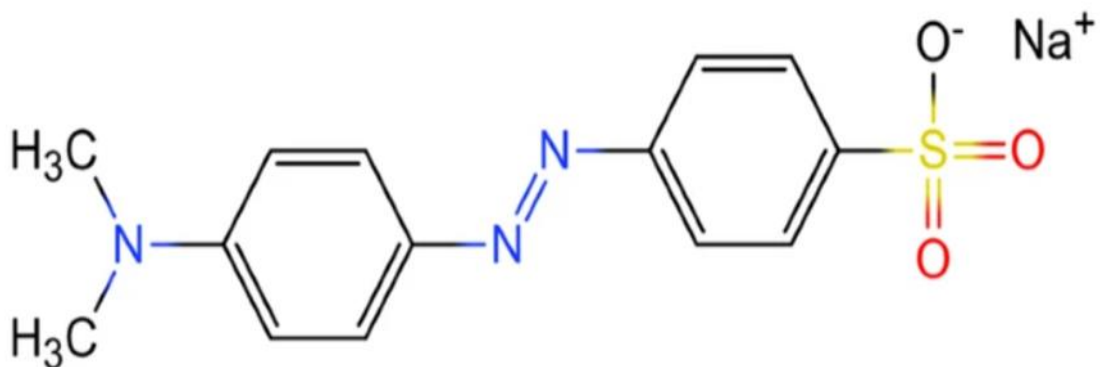


Figure 1.1: Molecular structural formula of methyl orange (Wu, L et al., 2021).

1.3 Nanomaterials

Nanomaterial is generally known as any material with at least one of its structures appeared in nanoscale dimension externally. According to ISO/TS 80004-2: 2015,

nanomaterials can be defined any material in nanoscale ranging from 1nm to 100nm. The ranging of the scale can be neither in the surface structure nor in the internal structure. Basically, nanomaterials can be separated into multiple distinct categories of nano-objects. They are the number of the dimensions limited at nanoscale and can be known as zero-dimensional (0-D), one-dimensional (1-D) and three dimensional (3-D). In 0-D nanomaterials, all the three-dimensional lengths are appeared apparently in nanoscale and commonly known as the nanoparticles or quantum dots. In 1-D nanomaterials, the two external dimensions is usually in nanoscale and recognized as nanofiber. In 2-D nanomaterials, they are known as nanoplates and will have only one of the external dimensions being confined at nanoscale. For the 3-D nanomaterials, they are not restricted to the nanoscale in any dimensions. They can appear in various forms, includes bulk powders, nanowires, nanotubes.

Applications of nanomaterials have been greatly studied in recent years, especially in the field of communication, manufacturing, health and knowledge-based technologies. Therefore, it is important to have a standard to characterize nanomaterials. By doing so, the rapid growth in studying the nanomaterials can be retained as the ideas discussion and researches in nanomaterials is constantly facilitated.

Compared to a large number of other useful metal oxide nanostructures, such TiO₂, ZnO, and NiO. The fabrication and study of WO_x nanostructures have also gained prominence with the development of nanotechnologies. It gives off certain qualities that do not exist in bulk form such as increased surface-to-volume ratio, which allows more surface area for chemical and physical interaction. They are a well-studied material for photocatalysis which are now widely used in relevant industries. This is because the nanostructures' high surface-to-volume ratio greatly raises the effective surface area that is accessible for photocatalytic processes (Zheng et al., 2011).

1.4 Photocatalytic Reaction of Semiconductor Photocatalyst

As mentioned previously, several methods can be utilised to carry out the removal of organic pollutants. Photocatalysis were focused among the others in this work. Photocatalysis is a chemical reaction of a substances known as photocatalyst under the influence of light. To understand it in other perspective alternately, photocatalysis is referring to the activities of the electrons on the surface of photocatalyst in responsible for absorbing photons to trigger the chemical reactions.

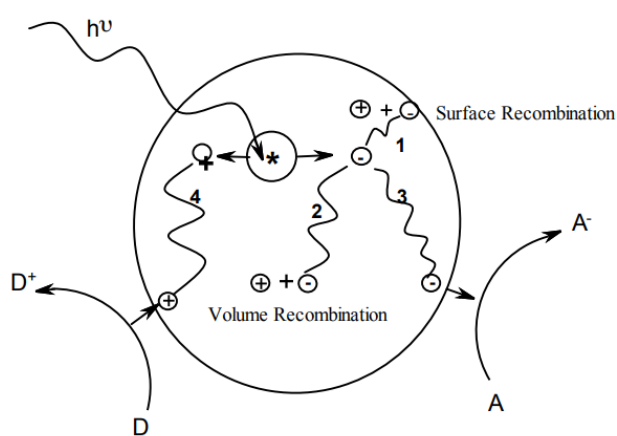


Figure 1.2: Schematic diagram of photoexcitation of semiconductor solid particle. (Yates, 2009)

In semiconductor photocatalytic reactions, electrons are excited from the valence band (VB) to the conduction band (CB) when photons are absorbed, and this results in the creation of electron-hole pairs on the surface of the semiconductor. (Yates, 2009) The photoexcitation of semiconductor solid particle is shown in Figure 1.2. The band gap between valence band (VB) and conduction band (CB) is the absolute energy needed. The photons are absorbed by the electron, which then creates an excited electron-hole pair. The electron-hole pair found can either move to the surface and recombine (1) or recombine in the volume (2). Some redox reactions, which is reduction (3) and oxidation (4) may be occurred on the surface of semiconductor within the electron-hole pair. (Chen and Mao, 2007).

Since 1981, heterogeneous photocatalysis has been a study field that has seen significant growth. This development has encouraged the elimination of environmental pollutants and can be achieved by illumination with photons using semiconductor materials. (Yates, 2009). Table 1.1 shows the band gap energy values of various semiconductor materials and Figure 1.3 shows the comparison among the semiconductor materials in terms of band gap energy diagram. (Zhiyong et al., 2008, Wang, 2009)

Table 1.1: Band gap energy values of semiconductor materials (Zhiyong et al., 2008)

| Photocatalyst | Band gap energy, electron volt (eV) |
|--------------------------------|--|
| Si | 1.1 |
| WSe ₂ | 1.2 |
| CdS | 2.4 |
| WO ₃ | 2.4-2.8 |
| V ₂ O ₅ | 2.7 |
| SiC | 3.0 |
| TiO ₂ Rutile | 3.02 |
| Fe ₂ O ₃ | 3.1 |
| TiO ₂ anatase | 3.2 |
| ZnO | 3.2 |
| SrTiO ₃ | 3.2 |
| SnO ₂ | 3.5 |
| ZnS | 3.6 |

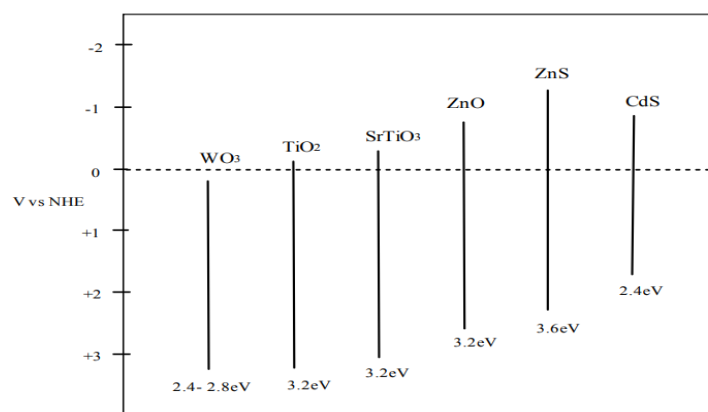


Figure 1.3: Band gap energy diagram for semiconductor materials. (Wang, 2009)

Methyl orange (MO) can be effectively degraded using advance oxidation process (AOP). With ultraviolet (UV) light, a photocatalyst and air, photocatalytic oxidation can be used to degrade MO. The photodegradation efficiency can be significantly enhanced by catalysts such as WO₃ (Mohammad et al., 2013). With that being aid, WO₃ can produce photoinduced electron/hole pairs when exposed to appropriate ultraviolet (UV) light source, which can start a chain of chemical processes that will eventually breakdown the contaminants (Zha et al., 2015). The production of many radicals and the molecule electrostatic attraction between the catalyst surface are two benefits of photocatalysis. Two primary steps of AOPs are the production of powerful oxidants (often hydroxyl radicals) and their interaction with organic contaminants in water. Photocatalytic oxidation involves direct photolysis, which occurs when UV light interacts directly with molecules without the use of chemical reagents. This leads to homolytic or heterolytic breakages in the molecules. The molecule will be transmitted from fundamental state to excited radicals state. The radicals can be broken down into a variety of organic substances, including water, CO₂, and mineral salts (Shirini et al., 2021)

1.5 Problem Statement

As mentioned, organic pollutant such as dye has posed serious environmental problems. Organic pollutants may need more time than expected to be completely degraded. Implementation of the nanotechnology in wastewater treatment has been a promising approach to replace the traditional wastewater treatment especially for total removal of dye molecules from water. Nanomaterials have high surface areas and hence would be able to absorb dyes from contaminated water. Photocatalytic nanomaterials such as oxide semiconductor, as mentioned above, would be able to absorb then degrade the MO molecule to less harmful products. This would allow for cleaner wastewater that is safe to be discharged to the environment.

Nanomaterials with different 1-D structure can be synthesized using various methods. Performance of each nanomaterial will be highly depending on the structure formed through different synthesis methods. Controlling the nanostructures is always the strategy to maximize photocatalytic process. Among various methods that can be used to produce nanomaterials, thermal oxidation of metal is one process that has not been explored greatly. Specifically oxidation of tungsten for nanostructured WO_3 and for the use of this oxide as photocatalyst to degrade MO. Conditions to produce oxide nanowires by thermal oxidation were explored here.

The feasibility study on nanostructured WO_3 for MO dye degradation is yet to be explored as there are limited amount of work on this despite the oxide is known to be photoactive. Therefore, this study aimed to synthesis on nanostructured WO_3 using thermal oxidation of tungsten, WO_3 , then on finding the efficiency to remove MO dyes in stimulated wastewater.

1.6 Research Objectives

1. To synthesis nanostructured tungsten oxide (WO_3) by using thermal oxidation method.
2. To investigate the possibility of MO removal in stimulated wastewater using the synthesized nanostructured WO_3 through photodegradation.

1.7 Scope of Research

In this research, thermal oxidation temperature of nano-structured WO_3 formation were using one-step and two-step thermal oxidation. The first process is carried out to synthesis nano-structured WO_3 via thermal oxidation on a pre-treated tungsten foil under a condition where both deposition of 2.0M potassium hydroxide (KOH) and thermal oxidation of tungsten carried out concurrently. Another one-step thermal oxidation was done with only annealed in normal atmospheric condition without the KOH. For the two-step thermal oxidation, it was carried out initially with deposition of 2.0M potassium hydroxide at 200°C for 0.5 hour to 2 hours, further continue on thermal oxidation at 400°C for 2 hours. Optimum distribution of the nanostructured WO_3 will be focused. The mechanism on the formation of nanostructured- WO_3 were studied. Selected samples were gone through Field Emission Scanning Electron Microscope (FESEM) and Energy-dispersive X-ray Spectroscopy (EDX) to be characterized and examined the growth of nanostructured WO_3 . Sets of samples were selected to be studied X-ray Diffraction Analysis (XRD). For the second section of the research, the degradation of Methyl Orange (MO) was studied through photocatalytic degradation under ultraviolet (UV) radiation using the synthesized nanostructured WO_3 on a thin tungsten film. The degradation of 10ppm of Methyl Orange (MO) solution was investigated with UV radiation to understand the photocatalytic performance of the synthesized nanostructured

WO₃. The degradation efficiency was studied by observing the colour saturation of the MO solution and ultraviolet-visible (UV-vis) spectrometry.

1.8 Outline of Chapters

This thesis consisted of five chapters. Chapter one explained the general introduction for the thesis, includes the introduction of dyes and its impacts, problem statement, objectives and scope of research of this work.

In Chapter Two, literature review and photocatalytic activities of nanostructured WO₃ were discussed. Chapter Three composed with the materials, chemicals, apparatus and instrument used, as well as methodology. This included the design of experiment and synthesis process of nanostructured WO_x by one step and two steps thermal oxidation. Other than that, the characterization techniques used, such as FESEM, XRD and UV-vis spectrophotometer is

On top of that, Chapter Four discussed the characterization results and analysis of WO_x film via thermal oxidation. At last, Chapter Five concluded this research work with recommendations were provided for future improvement.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

WO₃ is a well-known transition metal oxide used in photocatalytic application (Liao, Chen, and Kai 2007). The use of nanostructured WO₃ has greatly increased steeply over the years as the WO₃ has excellent photocatalytic properties. Due to the highly efficient absorption bands, band gaps, and surface areas, WO₃-based photocatalysts are found to be more effective for photocatalytic degradation. The improved photocatalytic properties of WO₃-based photocatalysts are examined for various pollutant removal methods, including the removal of synthetic and actual industrial effluent, among other pollutants. Yet, the properties can be unstable when WO₃ is in the form of film. In order to overcome this issue, researchers had been focusing to overcome this issue. They found out that nanostructure could be the key feature that affecting the photocatalytic performance of tungsten oxide. Throughout the researches, 1-D WO₃ nanostructures like nanotubes, nanofibers, and nanowires as well as mesoporous (Heo et al. 2017), nanoporous (Ng, Razak, and Lockman 2015a), and nanoflowers (Bhosale et al. 2017) and 1-D WO₃ can achieve better photocatalytic performance because they all have large surface-to-volume ratios. Due to the presence of dangling bond at the materials' surface and effect of surface curvature, 1-D nanomaterials are very reactive.

There are various ways in producing 1-D nanomaterials. However, most of the design of experiment will require expensive equipment and apparatus. Another reason is due to complicated synthesis methods. Among those methods, thermal oxidation is one of the most promising and easiest method for producing 1-D WO₃ nanostructure. To produce 1-D WO₃ nanostructure via thermal oxidation, a few works have been done.

There have been attempts to produce nanostructured WO_3 by oxidation of W in the presence of oxides or halides at elevated temperatures (Qi, Wang, and Liu 2003). The formation of 1D nanostructures frequently occurs within the framework of either vapour-solid (VS) or vapour-solid-liquid (VSL) processes and is catalysed by halides or oxides.

2.2 Importance of semiconductor photocatalyst in resolving dye pollution

The major issue of water contamination has affected the entire world. Large-scale groundwater pollution is the result of inadequate investments in the preservation of water resources. Additionally, the levels of numerous chemicals in groundwater have greatly surpassed the allowable limits. One of the main sources of wastewater is dye wastewater, which has high concentrations, large chrominances, and significant variations in water quality. As a result, it is challenging to effectively treat polluted water using conventional methods. Large amounts of dye wastewater are produced during the printing and dyeing process, which involves the physicochemical processing of numerous textile ingredients (fabrics, fibers, yarns, etc.). Nevertheless, the majority of dye wastewater contains biologically hazardous organic materials that can cause mutagenic, teratogenic and carcinogenic consequences. As such, Organic dyes have long been recognised as one of the most significant obstacles in the way of efficacy and efficiency of water pollution management and treatment processes. Therefore, the contamination of dye wastewater has become an important problem that needs to be resolved everywhere in the world.

In order to resolve the dye wastewater pollution, the latest solution is using the semiconductor photocatalyst to degrade the organic dye pollutant existed in the wastewater. Over the course of many years, studies on the utilizing the semiconductor oxide, such as titanium dioxide (TiO_2) (Wang et al., 2020, Xie et al., 2018, Cruz et al.,

2017), zinc oxide (ZnO) (Moazzen et al, 2013, Jaswini et al., 2016), (Vanitha et al., 2015), copper oxide (CuO) (Umadevi et al., 2013, Scuderi et al., 2016), to degrade organic pollutant has been greatly increased. In comparison among other semiconductor photocatalysts, tungsten oxide (WO_3) has managed to acquire relatively less exploration due to its indirect band gap energy. It had demonstrated enhanced responses toward the electromagnetic spectrum and had the potential to act as a catalyst in the photodegradation of contaminants. Moreover, the inertness to chemical action is one of the features of WO_3 , along with fine metal interaction, outstanding photoelectrochemical (PEC) properties, chemical stability across a wide pH range, and mechanical strength. Having of these highly efficiency properties, WO_3 finds widespread application in a variety of industrial applications, including sensors, dye-sensitized solar cells and photocatalyst. WO_3 is a visible light photocatalyst that has a band gap energy value that ranges between 2.4 and 2.8 eV. Correspondingly, WO_3 catalysts have negative surface charges, making them suitable for the absorption of cationic dyes, which is beneficial to photocatalytic reactions. Since the photocatalytic activities performances are greatly influenced by the nanostructure of WO_3 , WO_3 can come in several types of morphologies, such as nanoparticles, nanoflakes, nanowires and nanofibers.

2.3 Tungsten (W)

Tungsten (W) is a metallic transition element with atomic number of 74 and average atomic mass of 183.85. It is commonly known as wolfram. The application of tungsten is widespread, particularly found in a heater, cathode and in a variety of other electrical appliances, as well as present in a traditional filament lamp. Tungsten does not appear in its elemental form anywhere in nature. Conversely, it is always found bonded up with different forms of minerals. In terms of chemistry, tungsten is a

relatively inert metal that is capable of exhibiting resistance to a wide variety of elements and compounds. In frigid temperatures, tungsten is not affected by mineral acids, and it is very mildly affected even at higher temperatures. (Lassner and Schubert, 2012)

Among metals, tungsten is distinguished from other metals by having both the highest melting point and the lowest vapour pressure. Tungsten is a metal that is desirable for use in high performance applications. This is due to the fact that it has strong mechanical strength even when subjected to high temperatures. On the other hand, tungsten is prone to multiple types of corrosion, such as oxidation. This type of corrosion is increased at higher temperatures, which restricts how the high temperature capabilities of tungsten may be utilised (Lassner and Schubert, 2012).

Furthermore, tungsten exhibits a high degree of reactivity toward certain chemicals and agents. For example, tungsten is severely corroded by fluorine when it is at room temperature. Apart from that, tungsten reacts with a wide range of other reacting agents, including chlorine, phosphoric acid, potassium hydroxide, and sodium nitrate, when heated to an elevated temperature (250°C). When the temperature rises, the reaction speeds up and becomes more violent. (Lassner and Schubert, 2012)

2.4 Oxidation of tungsten (WO_x)

Tungsten is a very highly valued metal, particularly for high-performance applications. Nevertheless, tungsten has limited resistance to oxidation. This has caused pure tungsten restricted in vacuum or enclosed environment without any air molecules. Oxidation of tungsten has been extensively investigated. The oxidation of tungsten is affected by the thermodynamics and kinetics of all mechanisms that contribute to the production of oxide on tungsten (Lassner and Schubert, 2012). Lassner et al. has claimed that oxidation of tungsten is increased steeply at the temperature above 200°C.

As the oxidation temperature increased from 200°C, it will induce significant changes to the tungsten oxide. At the temperature above 750°C, an oxide layer will be formed. Tungsten oxide is known as a transition metal with wide variety of fascinating features, such as superconductivity and piezoelectricity (Hong et al., 2005). The classification of tungsten oxides species is shown in Figure 2.1 (Nilsson and Habainy, 2013). With a large number of complicated polymorphs and defect chemistry, the tungsten oxide family is a fascinating platform for theoretical and applied research, and it has been continuously explored in great details.

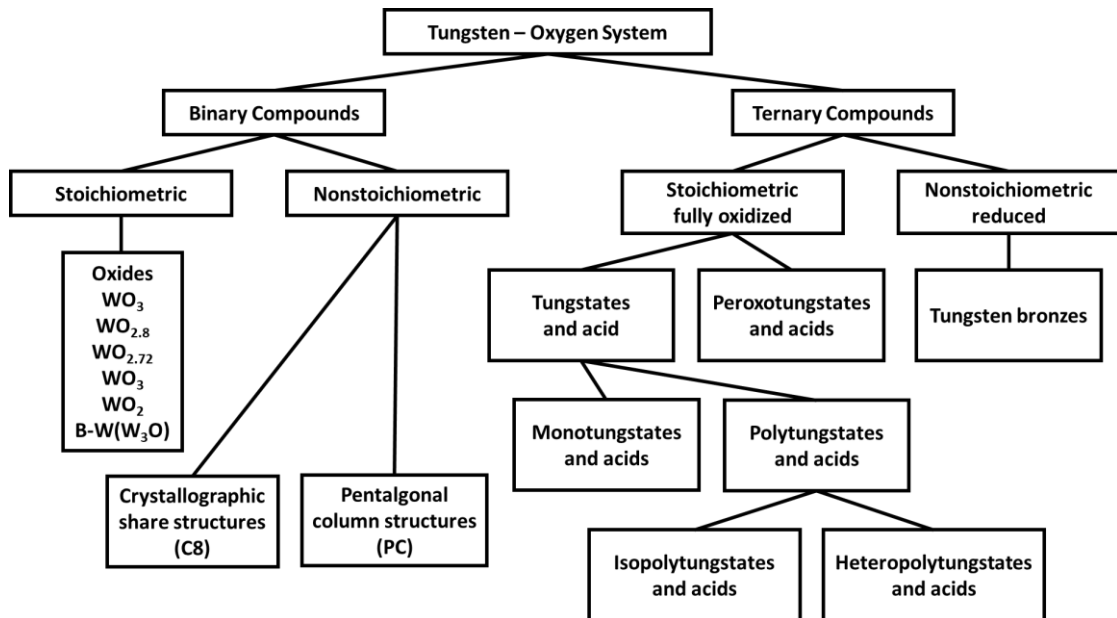


Figure 2.1: The compound system flow of Tungsten Oxide (Lassner and Schubert, 2012)

Many oxides phase of tungsten had been discovered. However, not all oxides phases are stable. The stable tungsten oxide namely WO_3 , $WO_{2.9}$, $WO_{2.72}$ and WO_2 . The colour in correspond with tungsten oxide is tabulated in Table 2.1.

Table 2.1: Tungsten Oxide in W-O system (Nilsson and Habainy, 2013)

| Stoichiometric Formula | O/W ration | Color |
|--|-------------------|-----------------|
| WO ₃ (α) | 3.00 | Yellow |
| W ₂₀ O ₅₈ (β) | 2.9 | Blue-violet |
| W ₁₈ O ₄₉ (γ) | 2.72 | Reddish- violet |
| WO ₂ (δ) | 2.00 | Brown |

2.5 Synthesis Methods of nanostructured WO₃ Photocatalyst

Throughout the years, nanostructured WO₃ can be synthesized by various methods, such as thermal decomposition (Inoue, 1995), sol-gel method (Shieh et al. 2002), pyrolysis (Bamwenda et al., 2001), ion-exchange method (Choi et al., 2002) and colloidal process (Sun et al., 2000). However, in this research will be focusing on the synthesis method using thermal oxidation, where this particular research works is found limited and less as mentioned before.

In the research work of Supothina et al., nanostructured WO₃ was synthesized through thermal oxidation using powder tungsten oxide, deionized water and cerium (Ce⁴⁺) aqueous solution. This suspension is then transferred to a reactor connected to a closed gas circulation system. The result shown was successful when the polycrystalline tungsten oxide nanowires structures was examined using transition electron microscopy (TEM). (Supothina et al., 2007)

2.6 Thermal oxidation of nanostructured WO₃

There have been variety studies reported that nanostructured WO₃ can be formed by various synthesis methods, including hydrothermal growth, evaporation-condensation growth, sol-gel method, template assist growth. Synthesis nanostructured WO₃ using thermal oxidation frequently needs temperatures above 700°C. However, there are a few studies reported on forming WO₃ using thermal oxidation method with temperature range below 500°C with or without the use of catalyst. As stated previously,

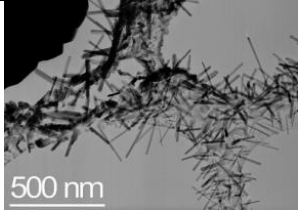
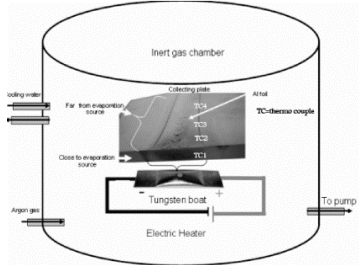
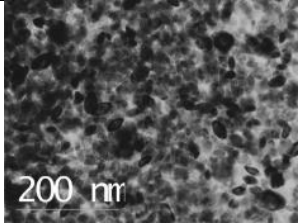
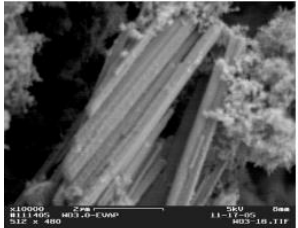
it is ideal to use oxides or halides as catalyst to aid in the growth of nanostructured WO_3 at lower temperatures.

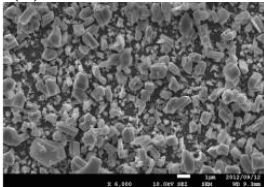
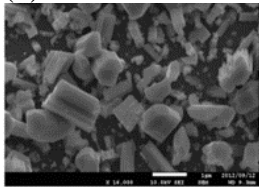
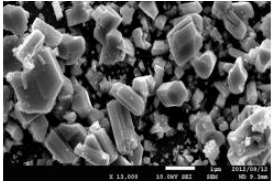
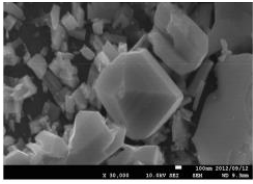
The thermal oxidation of tungsten can be classified into three different phases and each phase is controlled by unique mechanisms. The first stage of the oxidation takes place when the surface of the pure and exposed tungsten surface in contact with oxygen. This initial oxidation is regulated by phase boundaries. It does not depend on the diffusion up until the point where the oxide layer is fully covered the surface of tungsten. The oxide layer is commonly quite thin, but it is protective and adherent. In other words, this will prevent any further direct oxidation the pure tungsten beneath the oxide layer. This oxidation normally occurred below 400°C , obeying the general oxidation kinetics. The thickness formed of this oxide layer can be up until $0.1\ \mu\text{m}$ while the oxidation rate changes based on a particular parabolic rate law.

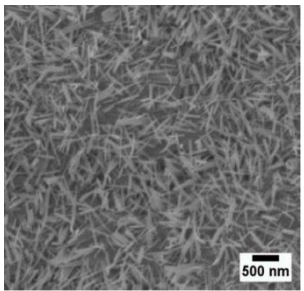
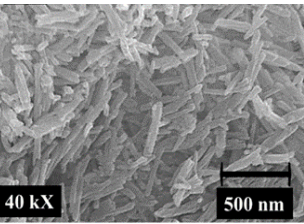
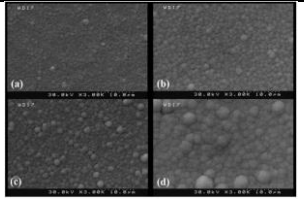
The growth of the first stage layer continues over 600°C in the second stage. This stage is regulated by diffusion, which happens when the tungsten is totally covered by an oxide at this point in the process. This oxide is made up of WO_3 , and it can be found in the most external layer, which has the highest concentration of oxygen. Its structure is distinct from that of the other oxides because it is porous and oxygen can easily pass through it. The movement of tungsten ions to the phase boundary where lower non-stoichiometric oxide meets WO_3 (Nilsson and Habainy 2013) is what determines the rate at which WO_3 is formed. However, the rate of growth of the WO_3 is dependent on the oxygen ion diffusivity in WO_3 because the oxide is an n-type semiconductor, which means that the oxygen ions are the ones that diffuse into the oxide. In other words, this means that the growth rate of the oxide is dependent on the oxygen ion diffusivity in WO_3 . (Nilsson and Habainy 2013)

Lastly, the third and final stage begin at the temperature of 750°C. The sublimation of WO_3 (Nilsson and Habainy 2013) begins to take place at temperatures higher than 750°C, at which point it also begins to have an impact on the properties of tungsten oxidation. When temperatures rise higher above 1300°C (Nilsson and Habainy 2013), the rate of sublimation is equal to the rate of oxidation. This indicates that there is no production of oxide on the surface since the oxide has entirely volatilized. The oxygen pressure has a significant impact on the oxidation of tungsten at these temperatures (Nilsson and Habainy 2013), and the volatilization of tungsten oxide also has an impact on the oxidation rate, both of which need to be considered carefully. However, in this study, the mechanism focused will be only on the first stage as the thermal oxidation temperature used was 400-600°C.

Table 2.2: Literature review on thermal oxidation of nanostructured-WO₃

| Author (year) | Oxidation Condition | Methodology | Morphology and Observation | | Mechanisms |
|--------------------------|---|---|--|---|---|
| Al-Sharab et al., (2009) | Temperature: <600°C Time: Not stated Environment: In a reduced pressure (0.5 torr) of high purity argon | In IGC, the WO ₃ powder is evaporated in a low-pressure vacuum chamber. The vaporized species collected on a water-cooled chill plate. The nanofibers formed can be collected at various locations on the chill plate. Elongated nanofibers are prevalent on the section of chill plate which is nearest to the evaporation source |  | WO ₃ nanofibers $\varnothing = \sim 30\text{nm}$ $\ell = \sim 400\text{nm}$ | <p>Thermal oxidation with inert gas condensation (IGC) process</p>  |
| | | |  | Disk-shaped WO ₃ nanoparticles | |
| | | |  | WO _{2.9} nanorods $\varnothing = 30\text{-}200\text{nm}$ $\ell = 7\mu\text{m}$ | |

| | | | | | |
|----------------------------|--|--|---|---|---|
| Senthilkumar et al. (2014) | <p>Temperature: (a)400°C ; (b)450°C</p> <p>Time: (a)6 hours; (b)8 hours</p> <p>Environment: In oxygen and argon mixed gas atmosphere</p> | Using an indium tin (ITO) oxide coated glass substrates to grow thin films of tungsten oxide | (a) 400°C / 6 hrs  | 1-D nanostructure | <p>Thermal evaporation technique</p> <p>Compared between two parameters to see which one is more suitable for gas chromic applications</p> <p>Parameter (a) only able to produce small crystallites than that in Parameter (b)</p> |
| | | | (b) 450°C / 8 hrs  | 2-D nanosheet | |
| | | |   | <p>3-D irregular and regular hexagonal nano prism structure of WO₃</p> <p>$\ell = 1-3\mu\text{m}$</p> <p>Thickness: 10nm</p> <p>Breath: 1.0-1.5μm</p> | |

| | | | | | |
|---------------------------|--|--|---|---|---|
| Zappa et al (2015) | <p>Temperature: 550°C</p> <p>Time: 1 hour</p> <p>Environment: In tube furnace with 0.8 mbar atmosphere pressure and 2 sccm oxygen flow</p> | Different thickness of tungsten foils was sputtered at various temperature to obtain optimum condition to grow WO ₃ NWs |  | <p>WO₃ nanowires</p> <p>Ø = <40nm</p> <p>ℓ = 10-35nm; 20-70nm</p> | <p>Plasma based Deposition</p> <p>Distribution of WO₃ NWs is the greatest when W foil with 180nm and sputtered at 300°C is used</p> |
| Behera and Chandra (2018) | <p>Temperature: 500°C</p> <p>Time: 4 hours</p> <p>Environment: In tube furnace under atmospheric ambient</p> | Pre-polished tungsten foils were deposited on SiO ₂ coated Si substrate |  | <p>WO₃ nanorods</p> <p>Ø = ~80nm</p> <p>ℓ = ~400nm</p> | <p>RF sputtering technique</p> |
| Yin et al., (2020) | <p>Temperature: 300-600°C</p> <p>Time: 2 hours</p> <p>Environment: In horizontal quartz tube</p> | Black thin layers of nanostructured-WO ₃ were deposited on a surface of an alumina substrate |  | <p>Cauliflower-like nano-structured WO₃</p> <p>Size: 5µm</p> | <p>Electron beam evaporator technique on substrates, followed by oxidation and evaporation</p> |

2.7 Fundamental of Photocatalysis

Photocatalysis is an approach that combines photochemistry and catalysis. In this approach, it implies that light and a catalyst are required to produce a chemical reaction. When the semiconductor photocatalyst involved in the process of photocatalysis, the surface of the semiconductor provides a stable environment for influencing the chemical reactivity of a diverse range of adsorbates and a means to initiate light-induced redox reactivity in these tenuously related molecules (Mohammed et al., 2019). Thermodynamic equilibrium occurs at the interface between an intact semiconductor and an aqueous solution. This may result in the formation of a space-charge layer within a small portion of the surface of semiconductor in the cases of p- and n-type semiconductors, where the electronic energy bands are typically downwardly or upwardly rotated respectively. The thickness of space-charge layer is normally at the range of $1-10^3$ nm and highly depends on the carrier density and dielectric constant of the semiconductor being used. The electron-hole pair would be generated and parted within the space-charge layer when the semiconductor detects the photons with energies greater than the band gap energy of the particular material. (Mohammed et al., 2019)

2.8 Semiconductor Photocatalyst – Tungsten Oxide (WO₃)

The interest in exploring tungsten oxide had started since 18th century from discovering the tungsten ore minerals, wolframite [(Fe₂Mn) WO₄]. The discovery of tungsten oxide continues and becomes more intense, especially in discovering the possibilities of this n-type transition metal oxide semiconductors. Tungsten oxide possess energy band gap of 2.8 eV. It had become a promising semiconductor in photocatalysts, photochromics and phototherapy. Due to its photocatalyst characteristic,

tungsten oxide has been proved that it has good absorption in visible light, either under domestic light source or using ultraviolet light radiation, as well as sunlight radiation. The stoichiometric compound of tungsten will have different appearance as the derivation took place. WO_3 has a number of different crystal structures, including the cubic, tetragonal, and hexagonal. WO_3 has the perovskite-type crystal structure and consists of WO_6 octahedra linked by corners and edge sharing as shown in Figure 2.2. The annealing and cooling temperatures of the oxide have a significant impact on the crystal phase of the WO_3 . (Zheng et al., 2011) WO_3 crystals undergo five phase transitions between 180 and 900 °C, shifting from tetragonal to orthorhombic to triclinic to monoclinic as they cool. (Saljie, 1977)

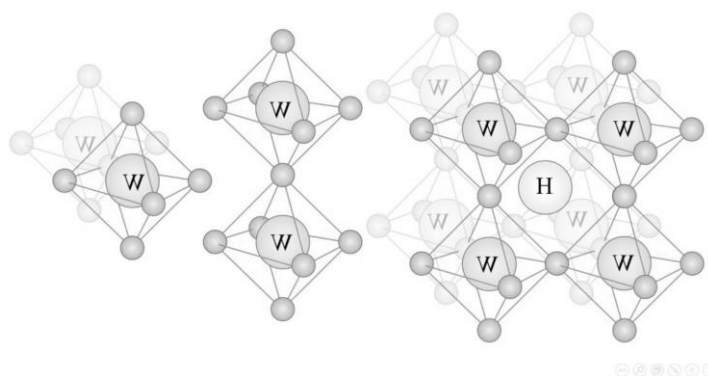


Figure 2.2: Structure illustration of (a) edge sharing octahedron (b) Corner-sharing octahedron and (c) WO_3 (Zheng et al., 2011)

2.9 Photocatalytic properties of nanostructured WO_3

As we have acknowledged, the researches are well documented on the capability of semiconductor photocatalysts to degrade a variety of pollutants at ambient pressure and temperature into less damaging compounds, such as hydrogen and carbon dioxide. Comparing semiconductors to noble metals, metal complexes, organic molecules, and ions, past researches have shown that semiconductors have superior photocatalytic performance, consistent cost, defined crystal structures, material toxicity, stability,