CHAPTER 1

Introduction

1.1 Photocatalysis

Since the discovery of synthetic dyes by W. H Perkins (1856) [1], the synthetic dyes have been used in a part of our daily life. However, these synthetic dyes could have many adverse effects on all form of life both in direct and indirect ways, for example, acute and chronic effects on exposed organisms, high visibility, and inhibiting an entering of sunlight in water [2]. There are several conventional methods to solve these problems, for instance, physical methods, biological treatments, and chemical treatments [2,3]. Unfortunately, these traditional methods lead to unpleasant side reactions which cause secondary pollutants, carcinogenic by-products, and/or toxic unstable metabolites [3]. Besides these attempts, heterogeneous photocatalytic process has been proved as an effective way to treat organic aquatic and atmospheric non-biodegradable contaminants utilizing the energy of either sunlight or artificial light sources [4–7].

In semiconductor photocatalysis, the photocatalytic process occurs when the semiconductors are irradiated with an energy equal or higher than their band gap energies resulted in the generation of excited electrons from valence band (VB) to conduction band (CB) (e_{CB-}), consequently, holes are generated in valence band (h_{VB}^+) (eq.1). The e_{CB}^- and h_{VB}^+ are strong reducing and oxidizing agents. Thus, the h_{VB}^+ reacts to organic molecules (R) and then produces small molecules (CO_2 and H_2O) as final products (eq. 2). Moreover, this active hole can also react with water molecules, or hydroxy anion to generate other active species, mainly, hydroxyl radical (•OH) (eq. 3,4). This generated •OH can non-selectively react with other electron-rich organic molecules and convert to CO_2 and water (eq. 5). In addition, e_{CB}^- can also generate superoxide radical ($O_2\bullet^-$) by reacting with absorbed oxygen molecules on the catalyst surface (eq. 6). After that, this $O_2\bullet^-$ can combine with proton, leading to the formation of peroxy radical ($\bullet OOH$). Further reaction between $\bullet OOH$ and e_{CB}^- in the presence of proton can produce hydrogen peroxide (H_2O_2) (eq. 7). This generated H_2O_2 can react with e_{CB}^- to form another hydroxy radical and hydroxy anion (eq. 8). Generated OH^- can further react with h_{VB}^+ to produce $\bullet OH$ (eq. 9). As a result, organic molecules are degraded by these reactive species [4]. TiO_2 and ZnO have been widely studied due to their high chemical stability, low cost, and excellent photocatalytic degradation of various organic compounds [6,8]. However, they do not show a good photocatalytic performance under visible light, the major part of sunlight, because of its wide band gap energy (> 3.0 eV) [6,9]. Therefore, many researchers have focused on developing other efficient photocatalysts to overcome this shortcoming.

$\text{Semiconductors} + hv \rightarrow e_{CB}^- + h_{VB}^+$ (1)
$h_{VB}^+ + R \rightarrow [\text{intermediates}] \rightarrow CO_2 + H_2O$ (2)
$OH^- + h_{VB}^+ \rightarrow \bullet OH$ (3)
$H_2O + h_{VB}^+ \rightarrow \bullet OH + H^+$ (4)
$\bullet OH + R \rightarrow [\text{intermediates}] \rightarrow CO_2 + H_2O$ (5)
$e_{CB}^- + O_2 \rightarrow O_2\bullet^-$ (6)
$\bullet OOH + e_{CB}^- + h_{VB}^+ \rightarrow H_2O_2$ (7)
$H_2O_2 + e_{CB}^- \rightarrow \bullet OH + OH^-$ (8)
$OH^- + h_{VB}^+ \rightarrow \bullet OH$ (9)

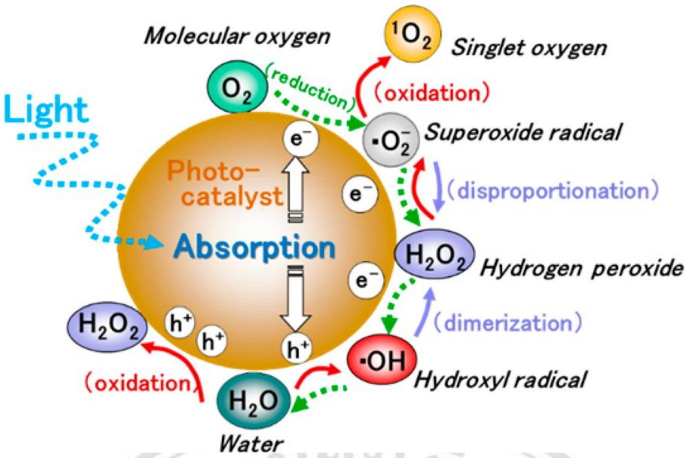

Figure 1.1 Reactive oxygen species generated in the photocatalytic reduction and oxidation steps of oxygen and water [10].

Nevertheless, the major factor affecting the efficient of photocatalysts is the probability of electron-hole recombination that can simultaneous occur when electron-hole pairs are generated as shown in Figure 1.2. This recombination process can reduce and inhibit photocatalytic process. Thus, the charge carrier recombination must be inhibited to improve photocatalytic performance. The valence band and conduction band are usually related to defects in the crystal. Therefore, generally, perfect crystals can reduce the recombination rate. Moreover, larger surface area of particles can also enhance photocatalytic performance due to better absorbing of organic molecules with increasing surface area of catalysts.

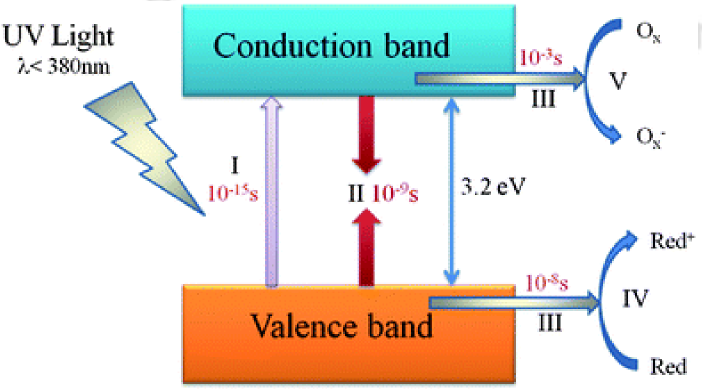

Figure 1.2 Primary steps in the photocatalytic mechanism (TiO_2) [11].

1.2 **Bismuth oxyhalide** [5,12,13]

Bismuth-based semiconductors have been considered as a promising candidate for solving both environmental and energy problems as the visible-light-responsive photocatalysts. With the disperse Bi 6s orbitals hybridizing with O 2p orbitals on valence band, the narrower energy band gap is usually achieved (less than 3.0 eV) while the valence band of commercial and traditional TiO_2 solely consists of O 2p orbitals. Among them, bismuth oxyhalides, BiOX (X = Cl, Br, and I), have shown potential as photocatalysts, mainly because of their optical and electrical properties. Moreover, they possess high stability, nontoxicity, and corrosion-resistant. The DFT calculation shows that the O 2p and X np orbitals (x = 3, 4, and 5 for X = Cl, Br, and I, respectively) dominate the valence band maximum of BiOX while the Bi 6p orbitals dominate the conduction band minimum. Therefore, the contribution of X np states increases as the atomic number increases, leading to narrow energy band gap. The energy band gaps of BiOX become narrower as the atomic number of halide ions increase; approximately 3.2 eV, 2.7 eV, and 1.7 eV for BiOCl, BiOBr, and BiOI, respectively (Figure 1.3).

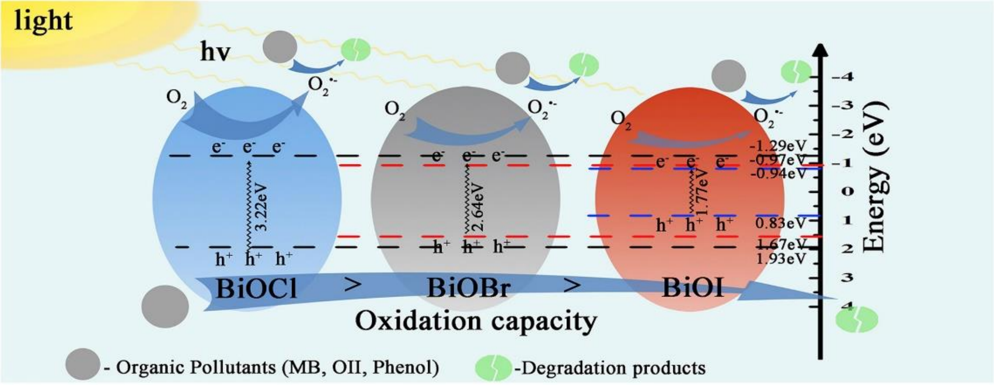

Figure 1.3 Valence band and conduction band positions and the energy band gap of BiOX (X = Cl, Br, I) [14].

Importantly, the crystal structure of BiOX consist of double layers of halogen atoms and interleaved with $[Bi_2O_2]$ slabs along [001] direction (Figure 1.4(a)). Notably, all BiOX compounds have tetragonal structure. The $[Bi_2O_2]$ layers are connected by covalent bonds, whereas the weak van der Waals forces are responsible for connecting [X] layers along the c-axis. The strong covalent interaction and weak van der Waals interaction induce to formation of open layered structure. The open-layer structure with non-uniform charge distribution between the halogens and [Bi_2O_2] slices intrinsically generates inherent internal static electric field (SIE) along the crystal structure, perpendicular to the [Bi_2O_2] and [X] slaps. As shown in Figure 1.4(b), the built-in SIE facilitates the separation of photogenerated electron-hole pairs which consequently benefits photocatalytic activity.

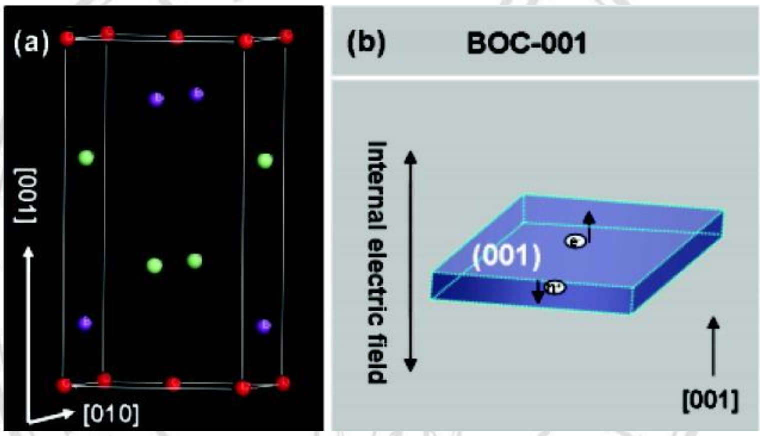

Figure 1.4 (a) Crystal structure of BiOCl. (b) Model showing the direction of the internal electric field in BiOCl with (001) exposed facets [15].

1.3 **Bismuth-rich strategy** [16,17]

Despite many potential applications of bismuth oxyhalide photocatalysts, their valence band and conduction band still possess low redox properties, consequently, limit their photocatalytic properties which relate to their band edge potentials. As mentioned before, the maximum valence bands of bismuth oxyhalide primary compose of both O 2p and X np orbitals (n = 3, 4, and 5 for X = Cl, Br, and I) orbitals while Bi 6p orbitals dominate the conduction band minimum. Therefore, adjusting atomic contents of BiOX materials can consequently modulate their band edge potential. According to thermodynamic aspects, the more positive the VB maximum, the stronger the oxidizing ability of holes. On the contrary, the electrons with higher reducing ability are generated with more negative CB minimum. To achieve this goal, dehalogenated BiOX ($Bi_xO_yI_z$) are synthesized to possess more negative CB and more positive VB than those with stoichiometric composition, as shown in Figure 1.5. Moreover, all bismuth-rich compounds exhibited higher photocatalytic degradation of bisphenol A in comparison to their stoichiometric parents (Figure 1.6), as a result from higher redox properties of photogenerated electron-hole pairs. The enhancement of electron migration and more efficient separation of electron-hole pairs resulted from hybridization of conduction band also facilitate photocatalytic activities of the bismuth-rich compounds.

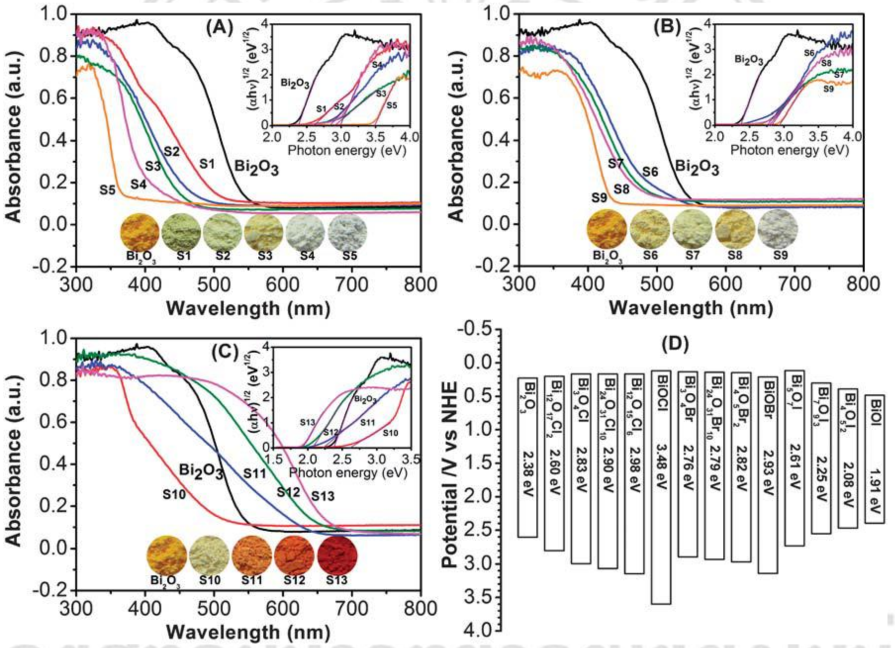

Figure 1.5 (a-c) UV-vis diffuse reflection spectra (DRS) of Bi_2O_3 and as-synthesized bismuth oxyhalides, the inset shows the plots of $(\alpha h\nu)^{1/2}$ *vs.* photon energy ($h\nu$), and (d) comparison of the band structures of Bi_2O_3 and bismuth oxyhalides [18].

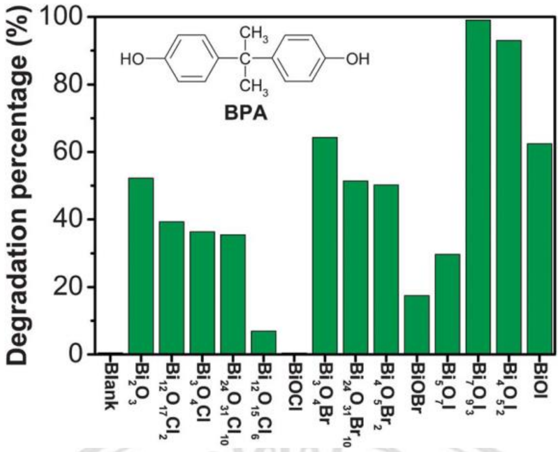

Figure 1.6 Degradation of bisphenol A (BPA) using blank (no catalyst), Bi_2O_3 and as-synthesized bismuth oxyhalides as photocatalyst, respectively, under visible-light irradiation for 2 h; inset shows the chemical structure of BPA [18].

1.4 Semiconductor-Semiconductor Heterostructures

The composite fabrication can be divided into three types (Figure 1.7); type I, II, and III, according to the band positions of two semiconductors [19]. In a type I heterostructure, the valence band (VB) of semiconductor A is higher than VB of semiconductor B while the conduction band (CB) of semiconductor B is lower than that of semiconductor A. Thus, the photogenerated holes and electrons can be transferred from VB(B) to VB(A) and CB(B) to CB(A), respectively. This phenomenon results in an accumulation of charge carriers, thus no improved photocatalytic activity is observed. Type II heterojunction provides an optimum band positions between these semiconductors. Under irradiated light, the photogenerated holes are transferred from VB(A) to VB(B) due to a larger negative potential while the excited electrons are migrated from CB(B) to CB(A) and thus separated from holes. As a result, the recombination probability significantly prohibits and, consequently, increasing electron-hole lifetimes. In type III heterojunction, the band positions are now entirely overlap, and such band positions are even further set off. However, the charge migration manners are as same as in type II heterostructures. This heterostructure might become so extreme that the bandgaps cease to overlap. Such arrangements of band structure are sometimes called broken-gap.

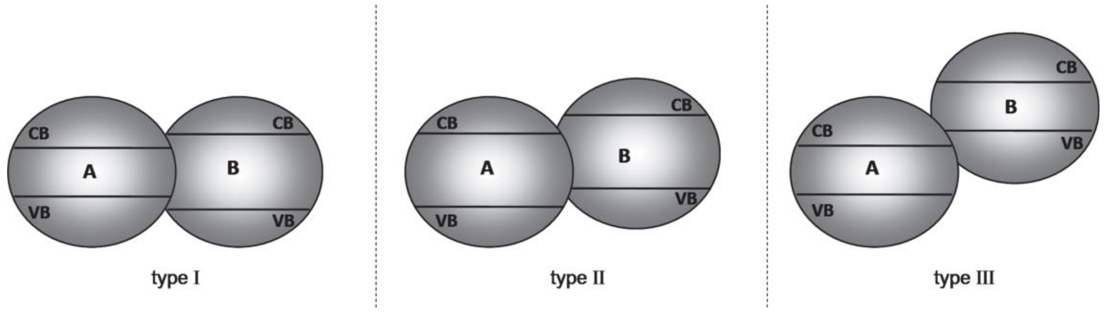

Figure 1.7 Diagrams illustrating the different types of heterojunctions [19].

1.5 Z-scheme heterojunction [20,21]

Inspiring by the natural photosynthesis process, the combination of two semiconductors for imitating this process is constructed. In comparison to conventional type II charge transfer process, the Z-scheme system possess lower valence band position and higher conduction band positions, providing stronger oxidation and reduction abilities. The Z-scheme system can be divided into three types: (1) traditional Z-scheme photocatalysts; (2) all-solid-state Z-scheme photocatalysts; and (3) direct Z-scheme photocatalysts. The discovery and evolution of Z-scheme photocatalysts are shown in Figure 1.8(a).

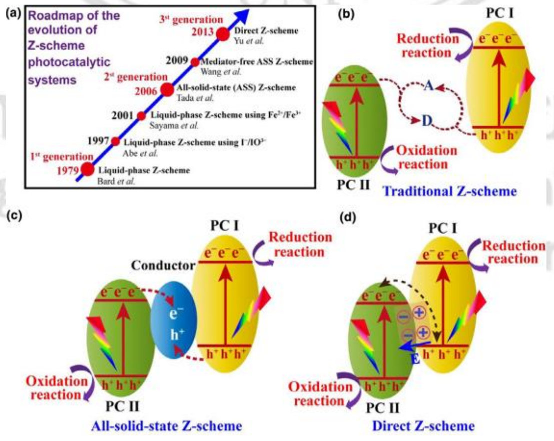

Figure 1.8 (a) The discovery and evolution of Z-scheme photocatalysts. Schematic diagrams of (b) Traditional Z-scheme process (c) All-solid-state Z-scheme process, and (d) Direct Z-scheme process [20].

1.5.1 Traditional Z-scheme photocatalysts

In this system, the redox mediator such as Fe^{3+}/Fe^{2+} is inserted between two different semiconductors which acts as an electron transfer chain. However, as the photogenerated holes and electrons have high redox power, the redox mediator can induce reverse reaction which is thermodynamically favoured by reacting with the photogenerated electron-hole pairs. Moreover, the diffusion of redox mediator limits the charge transfer process, consequently, affect the application of this traditional system. The charge transfer and reaction mechanism in the traditional Z-scheme system is shown in Figure 1.8(b).

1.5.2 All-solid-state Z-scheme photocatalysts

Similar to the traditional Z-scheme photocatalysts which require an electron mediator, an electron solid conductor acts in similar manner in all-solid-state Z-scheme photocatalysts (Figure 1.8(c)). The solid electron conductor can be novel metals such as Au, Ag, and Cu, or other conductive materials (e.g., graphene, CNTs). The solid conductors are acceptably better than ionic redox pair due to an ability to inhibit back reactions. However, an optimum amount of electron conductor is required because an excessive loading may lead to shielding effect.

1.5.3 Direct Z-scheme photocatalysts

The direct Z-scheme photocatalysts is the latest system where an electron mediator is not required. Therefore, the drawbacks of both aforementioned two systems are eliminated. As shown in Figure 1.8(d), two semiconductors with staggered band structure are intimately contact. To construct direct Z-scheme system, types of semiconductors are needed to be known as the pre-requisite for the formation of internal electric field which significantly affect charge transfer mechanism. In case of coupling two semiconductors with similar work functions, p-type or n-type semiconductors, the built-in electric field facilitates the Z-scheme charge transfer process by promoting the recombination between electrons in the CB of one semiconductor and holes in the VB of another semiconductor (Figure 1.9). On the contrary, coupling p-type and n-type semiconductors to form p-n junction lead to the transfer of electrons form n-type semiconductor to p-type semiconductor, resulting in an internal electric field. The electron-hole transportation is consequently favoured rather than direct Z-scheme pathway (Figure 1.10).

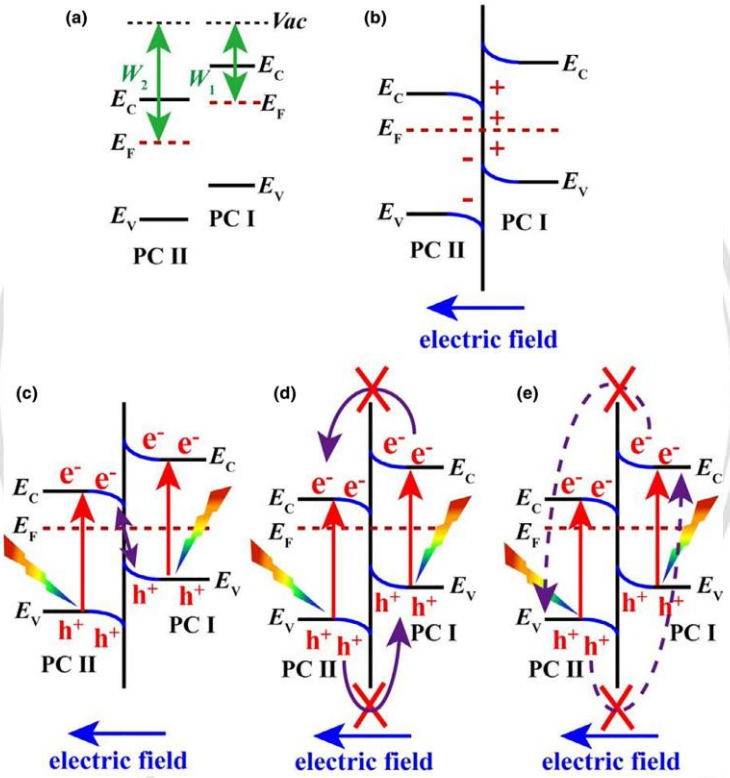

Figure 1.9 Schematic illustration of semiconductor-semiconductor with similar work function: (a) before contact, (b) after contact, (c) charge transfer process in Z-scheme mechanism, (d) charge transfer process in type-II mode, and (e) charge carrier recombination [20].

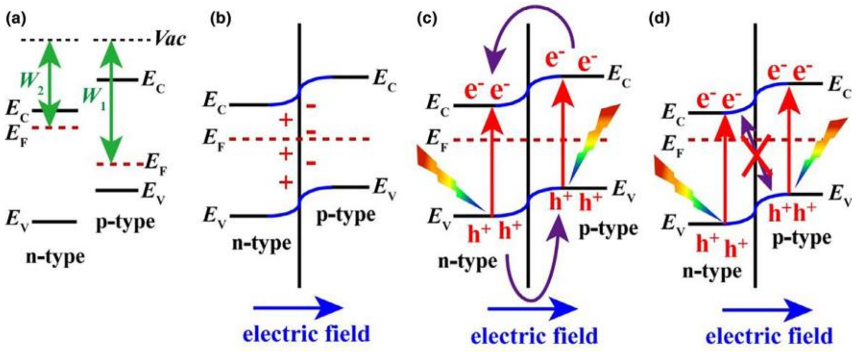

Figure 1.10 Schematic illustration of semiconductor-semiconductor with large different work function: (a) before contact, (b) after contact, (c) charge transfer process in type-II mode, and (d) charge transfer process in Z-scheme mechanism [20].

1.6 Microwave synthesis

Microwaves are a reliable and powerful energy source that has a wide range of applications. Microwave is an electromagnetic wave with a low frequency around 300 – 300,000 MHz and corresponds wavelength is about 1 centimetre to 1 metre. The various sources can generate different wavelength. Microwave consists of electric field and magnetic field that perpendicular to the x-axis as shown in Figure 1.11. Only electric field transfers an energy to the reactants and heat is generated.

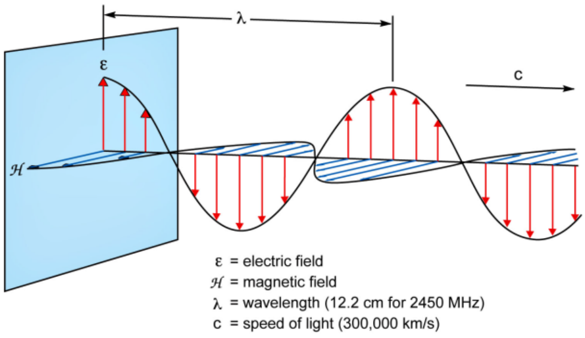

Figure 1.11 Electromagnetic wave [22].

1.6.1 Microwave irradiation method [23]

To study why microwave radiation can be used as heating source, it is necessary to understand the mechanism of microwave heating first. Microwave can be divided into an electric field which perpendicular to a magnetic field and these components are responsible for the dielectric heating via two major mechanisms.

1.6.1.1 Dipolar polarization or diploe rotation mechanism

This mechanism occurs when electric field interacted with substrates. The substrates, which can generate heat, must have a dipole moment, for example, water molecule. This dipole moment is very sensitive to an applied electric field and will align itself by rotation. The rotational motion is resulted in energy transfer to other molecules. So, any molecules with a dipole moment will encounter with this mechanism to generate heat.

In gases, molecules are freely packed, so the alignment is very rapid. In contrast, liquid molecules are tighter packed, and the rotation is prohibited by the presence of other molecules. However, the ability of alignment of liquid molecules are varied by frequency of microwave source and its viscosity. In microwave radiation, the applied frequency is low so that the dipole molecules can respond to applied electric field and therefore rotate. However, the microwave frequency is not high enough to make molecules precisely rotate follow applied electric field. Thereby, phase difference will occur and resulted in friction and collision which lost a generated energy and rise dielectric heating. For example, dioxane, low dipole moment molecule, cannot be heated by microwave radiation while water molecule, large dipole moment molecule, can be rapidly heated. So, that’s why gases molecules cannot be heated by microwave because the distance between adjacent molecule is very long and the molecules are able to perfectly follow the electric field, so no phase difference occurs.

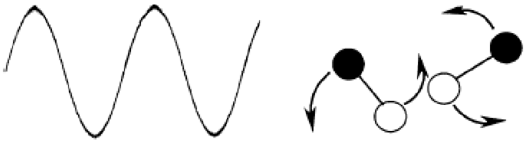

Figure 1.12 Dipolar molecules which align itself with an applied electric field.

1.6.1.2 Ionic conduction mechanism

The second mechanism is the resulted of free ions or charged particles in the heated substance. The electric field will generate a motion of ionic or charged particles that orient themselves to the applied electric filed. Thus, collision occurs and converting from kinetic energy to heat. This mechanism is much stronger than the dipole mechanism regarding to the heat-generating capacity.

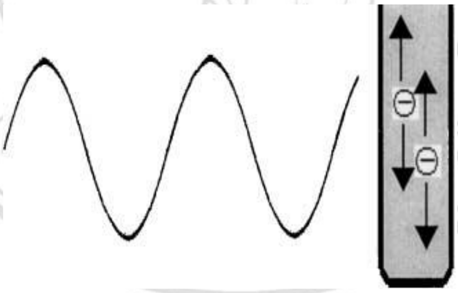

Figure 1.13 Charged particles in a heated substance following the applied electric field.

1.6.2 Solvents used in microwave synthesis [23]

Many factors affect the polarity and absorbing characteristics of solvent, for example, the dielectric constant, dipole moment, dielectric loss, tangent delta, and dielectric relaxation time.

1.6.2.1 The dielectric constant (ε')

The dielectric constant (ε') or relative permittivity of a solvent is or relative permittivity of a solvent is store electric charges. It is the ratio between electric capacity of solvent filled capacitor and evacuated capacitor. This factor depends on temperature and radiated frequency.

$$\varepsilon' = \frac{C_{filled}}{C_{evacuated}}$$

1.6.2.2 The dipole moment

The dipole moment is the mathematically calculated by the following equation below.

$$T = pE \text{ or } \mu = Qr$$

where T = torque
p = dipole moment
E = field strength
μ = dipole moment
Q = charge
r = distance between charges

According to this equation, molecules with high dipole moment also have high dielectric constant. Because, the polarization depends on dipole rotation.

1.6.2.3 Tangent delta (δ)

The tangent delta or loss tangent is the ability of a substance to convert electromagnetic wave into heat. In addition, the tangent delta is described as an efficiency of the sample that convert microwave power into heat and determined as shown in the equation below.

$$\delta = \frac{\varepsilon''}{\varepsilon'}$$

where δ = Tangent delta

ε' = Dielectric constant

ε'' = Dielectric loss or complexed permittivity

Dielectric loss is an amount of transferred input energy to the sample. Thus, the solvent that has high dielectric loss can generate a large amount of heat. Dielectric constant is an ability to store electrical charges of particular solvent and affected by temperature and microwave frequency.

1.6.2.4 Dielectric relaxation time

Relaxation time is the needed time to transfer an input microwave energy into thermal energy.

In conclusion, solvent with high dielectric constant and tangent delta will be resulted in the high final temperature. For example, acetone and ethanol with a comparable dielectric constant and tangent delta are heated at the same environment and the resulted final temperature of ethanol is higher than acetone as shown in Figure 2.10.

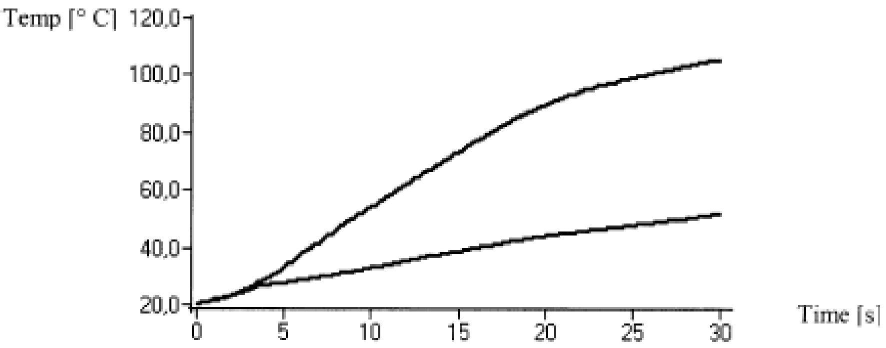

Figure 1.14 The temperature of ethanol and acetone. The upper curve is ethanol and the lower curve is acetone [23].

Table 1 Dielectric constant and tangent delta for some solvents (values determined at 2.45 GHz and room temperature) [23].

Solvent	Dielectric constant (ε')	Tangent delta (δ)
Propylene glycol	32.0	
Poly(ethylene glycol) 300	16.0	
Benzene	2.3	
Carbon tetrachloride	2.2	
Chloroform	4.7	
Acetic acid	6.1	0.091
Ethyl acetate	6.2	0.174
THF	7.6	0.059
Methylene chloride	9.1	0.047
Acetone	20.6	0.042
Ethanol	24.6	0.054
Methanol	32.7	0.941
Water	80.4	0.123
Ethylene glycol	37.0	1.350
2-propanol	18.3	0.799

1.6.2.5 Superheating effect

The dielectric constant and dielectric lose are relevant and dependent on relaxation time (τ). The relaxation time defines as the time it takes for one molecule to return to 36.8% of its original situation when the electric field is switched off. Thus, the ability of solvent to convert microwave energy into heat is not only depend on microwave frequency but also on the temperature. Thereby, solvent with a relaxation time >65 ps will have a lose tangent that increases with temperature and consequently increase the heating rate due to the limitation of the formation of “boiling nuclei”.

1.6.3 Comparison of microwave heating with conventional heating and the reason why microwave irradiation can enhance the rate of reaction [22,24]

Microwave can accelerate chemical reaction by giving rapidly transferred electromagnetic energy in 10^{-9} sec with each irradiated cycle whereas the kinetic molecular relaxation will take only 10^{-5} sec. Thus, energy transfer is faster than the molecular relaxation. Additionally, the lifetime of activated complexes is only 10^{-13} sec. However, there are some resonance-able compounds which have a longer lifetime than 10^{-9} seconds and resulted in polar species even ionic character which enhance microwave energy transfer.

The rate of reaction can be described by an Arrhenius rate equation.

$$K = Ae^{-\Delta E_a/RT}$$

where
K = rate constant
T = absolute temperature (Kelvin, K)
A = pre-exponential factor, a molecular mobility
E_a = activation energy of the reaction (Joules, J)
R = gas constant

Microwave energy will affect reaction temperature. An increasing of temperature will consequently increase rate constant and reaction rate which is the result of higher collision probability.

To sum up, traditional heating is using external heating source and the generated heat pass through the wall of vessel. In contrast, microwave radiation can heat the substrate from inside by interacting with present dipole or charged molecules or ions and do not depend on thermal conductivity of the vessel as shown in Figure 1.15.

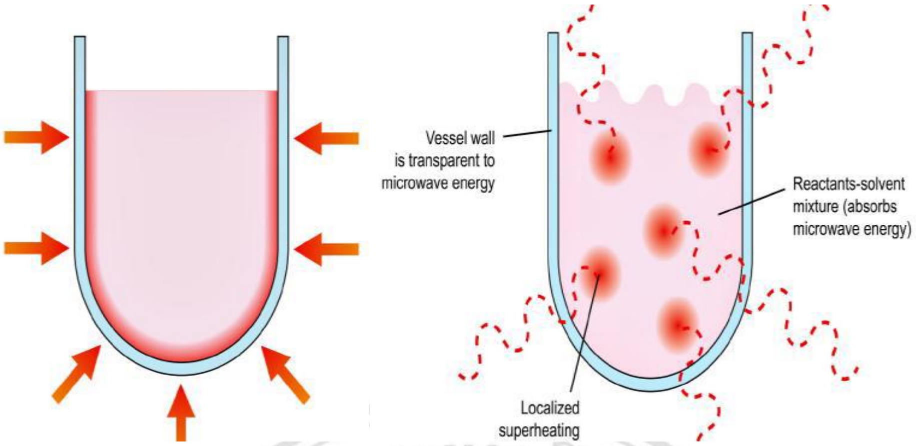

Figure 1.15 Sample heating; tradition heating (left) and microwave heating (right) [25].

Advantages:	Uniform heating occurs throughout the material
	Process speed is increased
	High efficiency of heating
	Reduction in unwanted side reaction
	Purity in final product
	Environmental heat loss can be avoided
Disadvantages:	Heat force control is difficult.
	Closed container is difficult because it could burst
	In-situ monitoring
	Expensive setup

1.7 Literatures review

With the overpopulation in the world, enormous of pollutants have been released into the environment [26]. Wastewater from the textile and dyeing industry are among the significant sources of organic pollutants, affecting the aquatic living lives in water, human beings, and ecosystems [27]. Semiconductor photocatalysis is considered as a potential technology to treat these problems, especially for the disposing of organic dyes [27]. TiO_2 and ZnO are the most widely used as photocatalytic semiconducting materials for water purification. However, they possess wide band gap energy so that limit the practical applications. They can only active with the UV light which occupies only about 5% of solar energy. Therefore, it is important to explore a suitable photocatalytic material that can harvest visible light, which is the major constituent of the solar spectrum (46%) [4,27,28].

Bismuth-contained materials catch considerable attentions due to their low toxicity, high natural abundant, high stability, and, especially, good photocatalytic activity under visible light irradiation [5,6,29]. Among them, bismuth oxyhalides (BiOX; X = Cl, Br, or I) have received much attention due to their unique intrinsic layered structure, and the corresponding optical and photocatalytic properties [5,6,30,31]. The layered structure consists of a layer of $[Bi_2O_2]^{2+}$ slabs interleaved by double slaps of halogen atoms. Such structure intrinsically generates a static internal electric field (SIE), efficiently promoting separation of the photogenerated electron-hole pairs [6,31]. BiOX photocatalysts have a wide range of applications, for example, photocatalytic oxidation activity for organic pollutants degradation [32–36], water splitting [37,38], photoreduction of CO_2 [39], nitrogen fixation [40], organic synthesis [41] as well as disinfection [42]. Nevertheless, the photocatalytic activity of these photocatalysts is suffered from its rapid electron-hole recombination rate as well as low conversion efficiency of solar light [43,44]. Many affords have been devoted to overcome these limitations such as morphology control [33,45], elemental doping [46–48], facet control [34,37,49], solid solution [50], surface decoration [51], synthesis of bismuth-rich compounds [52,53], and formation of heterojunction [54,55]. The valence band and conduction band are usually related to defects in the crystal. Therefore, generally, perfect crystals can reduce the recombination rate. Moreover, larger surface area of particles can also enhance photocatalytic performance due to better absorbing of organic molecules with increasing surface area of catalysts [56]. In particular, the fabrication of composite plays a crucial role in a semiconductor photocatalytic system which could highly increase surface area, improve light absorption, and increase charge carrier separation [16,19]. The suitable band positions between two materials facilitates an effective separation of photogenerated electron-hole pairs and rapid charge transfer, and thus improved photocatalytic activity [43,57]. Recently, a large number of BiOX-based composites have been widely synthesized such as $BiOCl/Bi_{12}O_{17}Cl_2$ [43], $Fe_2O_3/BiOCl$ [58], $BiOI/TiO_2$ [59], $BiOBr/BiVO_4$ [60], and so on. These studies reported that the heterostructures exhibited an enhanced photocatalytic activity compared to that of pure materials. Particularly, iodide-deficient bismuth oxyiodide ($Bi_7O_9I_3$) has attracted considerable interest in recent years as it has exhibited excellent visible-light driven photocatalytic activity for degradation of organic compounds such as colorless bisphenol A, phenol, and rhodamine B under visible-light irradiation [36,61,62].

Nanocrystalline $FeVO_4$ has recently received much attention because of its high chemical stability and catalytic selectivity [63]. It can be utilized in wildly applications such as organic pollutant degradation [64] and electrochromic electrodes [65]. Many publications reported that an enhanced photoelectrochemical (PEC) efficiency [63] and photocatalytic activities [66,67] of the $FeVO_4$-based composite resulted from an enhanced light absorption and charge carriers separation of the composite than that of single component. Herein, iron vanadate ($FeVO_4$) is chosen to combine with $Bi_7O_9I_3$ due to its distinct intrinsic properties, for example, a narrow energy band gap (about 2.1 eV) which can be activated under visible-light [66]. In addition, by considering the band gap energies and band positions of the $FeVO_4$ and $Bi_7O_9I_3$, it is possible that the photogenerated charge separation and charge transfer of $Bi_7O_9I_3$ could be improved by coupling with $FeVO_4$. Moreover, decorating semiconductor's surface with $FeVO_4$ nanoparticles could also lead to magnetically separable properties [68] and easily recover from a reaction system.

Synthesis methods such as hydrothermal [69,70], solvothermal [71,72], sol-gel [73], precipitation [74–76], reverse microemulsion [77], calcination [78], sonochemical methods [79], and microwave synthesis [32,80,81] have been applied to prepare the BiOX and $FeVO_4$ materials. Among these methods, microwave irradiation has proven to be an efficient way to synthesize nanomaterials due to its fast reaction, particularly, in minute scale, high yield, better reproducibility, energy saving, and homogeneous heating environment without heating temperature gradient [80,82–84]. The microwave heating involves two mechanisms which are dipolar polarization and ionic conduction. These two mechanisms are dependent on the properties of solvents, dipole moment and charge of polar species, and charged molecules, respectively. [25]. The ability of a solvent to absorb microwave energy plays an important role in microwave heating process [25]. Microwave radiation can create the interaction between chemical substances containing electric charges in order to generate internal heat during the reaction. The dipolar polarization and ionic conduction occur when an electric field interacts with dipole moment-contained substrates, such as water and ethylene glycol, and free ions or charged particles, respectively. The first mechanism results in rotational motion which transfers an energy to other molecules and finally generates heat. The second mechanism is the resulted of a motion of ionic or charged particles that orients themselves to the applied electric field. Thus, collision occurs and converts kinetic energy into heat. The resulting volumetric heating facilitates homogeneous nucleation, high reproducibility, and fine particle size with narrow size distribution of the final products [25,85]. In addition, short crystallization time, usually in minutes, and enhancement of reaction rate can be achieved. Moreover, many BiOX materials with high crystallinity, and complex porous hierarchical three-dimensional (3D) morphology, which facilitate light harvesting, and chemical adsorption, thus having a superior photocatalytic activity, can be synthesized through microwave heating method [80,81,86,87].

According to the above literatures, both $FeVO_4$ and $Bi_7O_9I_3$ photocatalysts will be first synthesized by microwave irradiation. After that, the $FeVO_4/Bi_7O_9I_3$ nanocomposite will be fabricated by a modified wet-impregnation method [88,89]. The effect of $FeVO_4$ loading amount in the $FeVO_4/Bi_7O_9I_3$ nanocomposite on their photocatalytic activities will be investigated by observing the decolorization of some organic dyes in aqueous solution under visible light irradiation. Up to now, to the best of our knowledge, synthesis of $FeVO_4/Bi_7O_9I_3$ composite and its photocatalytic applications have not been reported yet. The knowledge obtained in the present work will be useful for exploring other photocatalysts for dye degradation and photoelectrochemical properties.

1.8 Research objectives

1.8.1 To synthesize and characterize $FeVO_4$ and $Bi_7O_9I_3$ by a cyclic microwave irradiation method

1.8.2 To synthesize and characterize novel $FeVO_4/Bi_7O_9I_3$ composite by a wet-impregnation method

1.8.3 To study the effect of $FeVO_4$ loading on the photocatalytic activity of the $FeVO_4/Bi_7O_9I_3$ photocatalysts for photocatalytic degradation of dyes under visible light irradiation

1.9 Usefulness of this research

1.9.1 The knowledge from the improvement of the $Bi_7O_9I_3$ photocatalyst will benefit the removal of toxic chemicals in wastewater.

1.9.2 The microwave synthesis could also be used an alternative method for synthesizing inorganic materials with low energy and time consumption.