P-block-based Ferroelectric-photocatalyst compounds: Structure, Ferroelectric properties and photocatalytic performance

Amar Hadee Jareeze Al-Keisy

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P-block-based Ferroelectric-photocatalyst compounds: Structure, Ferroelectric properties and photocatalytic performance

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Dr. Yi Du & Prof. Shi Xue Dou

This thesis is presented as part of the requirement for the conferral of the degree:
Doctor of Philosophy

The University of Wollongong
Institute for Superconducting and Electronic Materials

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Abstract

The high recombination rates of photogenerated electron-hole pairs inside the bulk of photocatalyst, the back-reactions of intermediate species and inactive visible light are regarded as the key issues blocking solar light-conversion efficiency. P-block photocatalyst based-internal electric field compounds are regarded as a much attractive attention for photocatalysts because of their dispersive and anisotropic band structures, as well as their intrinsic internal electric field. The driving force of charges separation via internal electric field plays a key role to reduce recombination rates. In this thesis, it is divided into three parts by using three p-block photocatalyst based-internal electric field compounds:

Firstly, we have developed a new ferroelectric p-block photocatalyst, $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, by materials design and band engineering. $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ was synthesized by the solid ion-exchange method. It was found that $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ has excellent photocatalytic performance towards the degradation of dyes and phenol over the entire visible light spectrum. The reason behind the efficient activity of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is attributed to its narrow band gap, dispersive band structure and internal electric field which has proven theoretically and experimentally.

Secondly, construction unique bismuth silicate based 0D/2D heterogeneous nanostructures was synthesis by hydrothermal. This heterogeneous structure exhibited much enhanced photocatalytic activity towards the degradation of Rhodamine B and phenol. This work provides a novel strategy for adjusting the photoinduced carrier transfer route in the ferroelectric materials and designing novel photocatalysts with ultrafast charge separation and a large active surface area.

Finally, selective deposition BiOI on the positive polar $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by polarization-adsorption effect and evaluation of the photocatalytic performance. A complete photodegradation of RhB was obtained by a specific amount of BiOI interfacing with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in 12 min under visible light and 47% of phenol has been photodegraded within 1 hour. This is confirmed that selective deposition on the positive polar surface of ferroelectric produces higher photocatalytic activity rather than that random heterojunction.

Overall, the results were demonstrated that p-block photocatalyst based-internal electric field compounds exhibited excellent photocatalytic activity compare with non-p-block photocatalyst based-internal electric field. The p-block compounds own the unique $d^{10}$ and sp/p configurations in its electronic structure and also anisotropic and highly dispersive band structure whereas internal electric field produced spatially oxidation/reduction (redox) sites on surfaces due to own high charge separation, also, it can reduce the back-reaction on the surfaces.
Acknowledgments

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Finally, my thanks are for my parents, my wife, my brothers and my sister for their support and encourages throughout my study.

Amar Al-keisy
Certification

I, Amar Hadee Jareeze Al-Keisy, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree Doctor philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

____________________________
Amar Hadee Jareeze Al-Keisy
20th May 2018
List of Abbreviations

**Instruments group**
AFM: Atomic Force Microscopy  
EDS: Energy Dispersive X-ray Spectroscopy  
SEM: Scanning Electron Microscope  
TEM: Transmission Electron Microscope  
XRD: X-ray diffraction  
PFM: piezoresponse force microscopy  
AFM: Atomic force microscopy  
FESEM: The field emission scanning electron microscope  
UV-Vis spectroscopy: ultraviolet-visible spectroscopy

**Electrochemical group**
Ag/AgCl: Silver/silver chloride reference electrode  
NHE: Normal hydrogen electrode  
SCE: saturated calomel electrode  
Efb: flat-band potentials  
Pt: Platinum

**Calculation group**
GGA: generalized gradient approximation  
PBE: functional of Perdew, Burke, and Ernzerhof  
TMO: transition metal oxide  
DFT: Density functional theory

**Dye group**
CV: Crystal Violet  
MB: Methylene Blue  
MO: Methyl orange  
MB: Methylene blue  
RhB: Rhodamin B

**Different group**
TOC: Total Organic Carbon  
AOPs: Advanced Oxidation Processes  
CB: Conduction Band  
CNTs: Carbon Nanotubes  
UV: Ultra Violet  
VB: Valance Band  
Eg: Optical band gap of the semiconductor  
FTO: Fluorine-doped tin oxide  
TM: Transition metals
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Chapter 1

Introduction

1.1 Background and motivation

Because of the growing world population and increased economic growth, there has been an increase in water contamination by harmful substances and an increase in carbon dioxide in the air from burning fossil fuels. Moreover, fossil fuel resources are limited and will be restricted in the future, but fossil fuels are currently a source of air pollution and also playing a role in global warming, making the planet less liveable for people in future. The demand for global power is expected to rise by 30% between today and 2040 [1]. Moreover, by 2050, world population will much higher. Thus, wastewater will be doubled. Currently, global warming has led to warnings of disaster if there are no precautions take into consideration. Scientists and engineers around the world have been seriously concerned with these issues. Therefore, significant efforts have been made to develop techniques to eliminate these harmful substances, which produced by many sources, especially industry. It is well known that conventional methods (include adsorption, coagulation, flocculation, sedimentation, and bio-filtration) cannot degrade recalcitrant compounds [2]. Thus, some heavy metal ions and toxic organic compounds are still present in wastewater after treatment, even expensive treatment, and not meet the standards required for the population [3]. Alternative advanced technologies have been adopted and developed, such as advanced oxidation processes (AOPs) which have been shown to be promising techniques to break down the harmful chemicals in wastewater. They can remove and degrade a wide range of organic components by generating active species radicals. These species attack the organic pollutants in water and react with them to generate safe materials such as CO$_2$ and H$_2$O. This technique is considered as expensive for practical application, however, because it uses ultraviolet (UV) light and ozone or other oxidation species. A few decades ago, among the AOPs, the photocatalysis process received much attention as a technology to solve the energy crisis and environmental pollution, because this technique is based on solar energy, which is a permanent and clean source of energy as well, as it is environmentally safe and renewable.

Photocatalysis is defined as “a photoreaction that is accelerated by the presence of a catalyst.” Photocatalysts, such as TiO$_2$, have been demonstrated to have significant efficiency in degrading widespread recalcitrant toxic compounds [4-6]. 120,000 TW (~1000 Wm$^{-2}$) of the sunlight power strikes the Earth’s surface, which far exceeds the human demand for power and thus offers free and clean sustainable energy. The photocatalytic materials are not only applied in photodegradation and water splitting, but also have antibacterial, self-cleaning, and other applications. Hydrogen production from water splitting has been considered an attractive, to environmentally friendly, and sustainable source of energy. Until now, photocatalyst techniques for practical applications are still under challenge because of many limitations, such as high rates
of recombination of photoinduced carriers, wide band gaps, high cost, and instability. Therefore, the aims of this project were to develop, enhance, and explore photocatalysts to fulfill the requirements of practical application.

1.2 Fundamentals and mechanism of photocatalysis

Photocatalysis is a process in materials (including semiconductors, polymers, heterostructures, etc.) that is able to produce chemical modification or new products on the surface of photocatalyst materials by absorption of a photon of light. There are two principal steps in photocatalysis: in the first, the material, normally a semiconductor, is photoexcited to generate electrons and holes, and in the second, these photoexcited electrons and holes are involved in a series of chemical reactions. Among these photocatalysts are semiconductor-based photocatalysts. Semiconductor photocatalysts such as TiO$_2$ were widely studied in the past because of their chemical stability, superhydrophilicity, strong ability to oxidize organic pollutants, and nontoxicity.

The photocatalysis mechanism starts to work when a photon of light (wavelength, $\lambda_{ph} = 300$-700 nm) is absorbed that has energy ($h\nu$) greater than or equal to band-gap energy of a semiconductor, such as TiO$_2$ [4, 7-9], ZnO [5, 10-12], CdS [13], or WO$_3$ [14-16], and then an electron in valence band (VB) transit to conduction band (CB) (Equation (1.1)), thus leaving positive charge in the VB called hole [17, 18]. And then they (photoinduced electrons and holes) move to the surface of the photocatalyst, the reactions will occur between electrons and holes with previously adsorbed materials (such as H$_2$O, oxygen, and organic pollutants) to modify them or produce new chemicals. The electrons in CB ($e_{CB}$) act as reductive sites, whereas the holes in the VB ($h^+_{VB}$) act as oxidative sites.

$$\text{Photocatalyst} \xrightarrow{h\nu} e_{CB}^- + h^+_{VB} \quad 1-1$$

In the case where the photogenerated electron-hole recombines on the surface or inside the bulk of the photocatalyst, the photon energy will be dissipated by emission heat or photons. The photo-degradation of organic materials occur when powerful reductive/oxidative agents such as holes, OH•, O$_2$•$^-$, and H$_2$O$_2$ produced in water that generated from reaction holes and electrons with previously dissolved oxygen and water molecules adsorbed on the surface of photocatalyst (Equation 1.2). The schematic illustrations in Figure 1-1 shows the process in a typical photocatalyst [19]. In this case, the conduction band has a negative potential (i.e. reduction potential over 0 V vs. normal hydrogen electrode(NHE), and the valence band has a positive potential (i.e. oxidation potential over 1.23 V vs. NHE), so the photocatalyst can convert (Equations (1.2) and (1.3)) organic compounds and H$_2$O to CO$_2$ and H$_2$, respectively [20-22]. Otherwise, the photocatalyst can only oxidize organic pollutants. Thus, the hydrogen production or pollutant degradation strongly depends on the band and electronic structure of the photocatalyst.

$$\text{Organic compounds} \xrightarrow{\text{photocatalyst/} h\nu} \text{intermediate(s)} \rightarrow \text{CO}_2 + \text{H}_2 \quad 1-2$$

$$\text{H}_2\text{O} \xrightarrow{\text{photocatalyst/} h\nu} \rightarrow \text{O}_2 + \text{H}_2 \quad 1-2$$
Figure 1-1 Schematic diagram of a typical photocatalyst illustrates that the electrons transfer to the conduction band after absorbing light, leaving a hole in the valence band, and move to the surface to react with materials have previously been adsorbed on the surface.

Generally, the capability to hydrogen evolution or oxygen evolution is strongly depend on oxidation and reduction potential of VB and CB respectively. Thus, electronic and band structure are much important to photocatalytic activity. Moreover, there are many factors effect on photocatalytic activity such as shape and size particles and include internal electric field of photocatalyst.

The band structure is important to determine the band-gap ($E_g$) value and the CB and VB positions of a photocatalyst. The CB and VB arrangement for many photocatalysts is shown in Figure 1-2. From the Figure, in the case of hydrogen production, it is clear that the electron in the CB must be higher than the hydrogen reduction potential (0 V on the NHE scale), while the hole in VB must be below the oxygen oxidization level (1.23 V on the NHE scale) [22]. Materials design and band engineering can be used to modify the $E_g$, CB, and VB to absorb visible light in order to fully harvest solar light and also modify the CB and VB positions to achieve a favourable level of oxidation potential for the organic pollutants. Highly dispersive CB and VB bands cause the charge carriers to have much smaller effective masses, which facilitates charge transfer to surface. Moreover, the natural surface/interface properties of the photocatalyst play an important role in the photocatalytic activity, because higher surface energy leads to higher photocatalytic activity [23]. The charge carriers (electrons and holes) should diffuse to the surface of a photocatalyst in a time shorter than the average lifetime of the electron-hole pair, because otherwise they will recombine. Therefore, nanostructures offer short distances for the migration of electron-hole pairs to the surface, and the creation of a high surface area and increasing the density...
of reactive sites will also help. Reducing the size of particles cannot always increase their photocatalytic activity, however. Non-toxic and low-cost photocatalytic materials are also essential factors, as well as the stability of photocatalyst in a particular practical application. To overcome all these issues, many efforts were carried out to development, enhancement, and exploration photocatalysts [24, 25].

![Figure 1-2 Band-gap positions for photocatalysis in different semiconductors, and their capability to produce radical species and convert CO$_2$ to hydrocarbon compounds [26].](image)

### 1.3 Mechanism of photodegradation

One major danger facing the environment is pollutants, both organic pollutants and heavy metal ions. These pollutants are found in water and air, which are waste products coming from various industries. These pollutants kill marine life and damage the central nervous systems of animals. Some of these pollutants are highly toxic, such as phenolic compounds, fungicides, herbicides, dyes. It has been mentioned above that these pollutants cannot be removed by conventional methods and AOPs can be expensive. Therefore, photocatalysis processing, which is one of AOPs, is a promising technique to overcome pollution in the environment. It has been demonstrated completely that the degradation and mineralization pollutants can be achieved under solar light. The holes in the valence band can directly react with water to produce proton (H$^+$) and the hydroxy radical OH-. Then, OH- is converted to OH• by reaction with a hole. Also, the holes can directly react with pollutants in adsorbed water, whereas electrons in the conduction band can
produce superoxide radicals (O$_2$•−) by reacting with dissolved oxygen in water and also produce H$_2$O$_2$. The holes, OH•, O$_2$•−, and H$_2$O$_2$ are powerful oxidation species toward the degradation pollutants and other recalcitrant substances. Figure 1-3 shows a schematic illustration of the degradation process for pollutants (P) by photoinduced electrons and holes in TiO$_2$ [27]. These species attack organic pollutants in water, which leads to the decomposition and mineralization of pollutants to simple compounds such as CO$_2$ and H$_2$O. Unfortunately, the efficiency of the photocatalyst often cannot meet practical requirements because of certain limitations. The major limitations of a photocatalyst relate to its photocatalytic activity and stability. A high recombination rate in photoinduced charge carriers leads to high dissipation of light energy and thus reduces photocatalytic activity. The photoinduced charge carrier lifetime to reach the surface should be longer than recombination time. Besides wastage from the recombination of photoinduced charge carriers and instability, the reverse reactions occur on the photocatalyst surface because of reduction and oxidation sites in the same location on the surface [28], and the activity of the photocatalyst is also affected by the wettability of the surface.

![Figure 1-3 Schematic illustration of degradation process for pollutants (P) by photoinduced electron and hole in TiO$_2$ [28].](image)

It should be noted that all photocatalysts cannot produce highly oxidative species, in particular, those with a narrow band gap. The narrow-band-gap semiconductors have high absorption efficiency toward the visible spectrum of solar light. Nevertheless, the narrow band gaps do not always match with the redox capabilities of organic pollutants, and a wide band gap cannot absorb visible solar light, which represents 55% of solar light. For example, the CB must be more negative than the reduction potential of O$_2$ to form O$_2$•− (O$_2$•− /O$_2$ = -0.28 V vs. NHE at pH = 0), whereas the VB should be more positive than the oxidation potential of H$_2$O to form OH• (OH•/H$_2$O= +2.27 V vs. NHE at pH = 0). Generally, visible light active, low charge recombination, stability, low cost, and suitable band structure for oxidation and reduction potential
cannot all be achieved in a photocatalyst, so it remains a great challenge to apply photocatalysis in practical applications. Therefore, material design strategies and band structure engineering, as well as morphology control, have been adopted to meet the requirements of practical applications.

1.4 Photocatalysis applications

Besides pollutant degradation and hydrogen production [34-37], there are many other applications for photocatalysis, and the most important are listed below. Moreover, it is expected that there will be more applications in future. It should be noted that the ability to apply photocatalysis in a particular area mainly depends on the reduction and oxidation capability of the photocatalyst along with many other factors.

- Purification and disinfection of air and water
  Organic pollutants and microorganisms are destroyed when water molecules are decomposed under the solar light in the presence of a photocatalyst, producing free radicals which can destroy organic pollutants and microorganisms. The most commonly used photocatalyst in this application is TiO\(_2\), in the form of an ultrathin film of TiO\(_2\) coated glass. Outdoor air purification was achieved by coating buildings with TiO\(_2\) under solar light can decompose harmful gases in water such as H\(_2\)S and NO [29, 30]. Photoreduction of Cr (VI) by a photocatalyst has been achieved with complete photoreduction to Cr (III) which has little toxicity [31-34].

- CO\(_2\) and N\(_2\) fixation
  Photocatalysis is a promising technique to produce valuable solar fuels such as CO or CH\(_4\), and NH\(_3\) from CO\(_2\), water and N\(_2\) (Equations (1.4) and (1.5), respectively, because it is simple and uses solar light as its source of energy [21, 22, 35, 36]. Industrial production of NH\(_3\) requires high temperature and pressure in the presence of a catalyst, but photocatalyst can use solar light to produce renewable fertilizers under mild conditions. Photoreduction of CO\(_2\) is much more complicated than hydrogen production. Generally, converting CO\(_2\) to CH\(_4\) requires the participation of eight electrons and 8 holes, while converting N\(_2\) to 2NH\(_3\) requires the participation of six electrons and 6 holes. The band structure is very important for triggering the reaction, and the CB should be more negative than the reduction potential of N\(_2\) or CO\(_2\), whereas the VB should be more positive than the oxidation potential of oxygen evolution.

\[
\frac{1}{2}N_2 + \frac{3}{2}H_2O \xrightarrow{\text{photocatalyst/\(hv\)}} \rightarrow NH_3 + \frac{3}{4}O_2 \quad \ldots(1.4)
\]

\[
CO_2 + 2H_2O \xrightarrow{\text{photocatalyst/\(hv\)}} \rightarrow CH_4 + 2O_2 \quad \ldots(1.5)
\]

1.5 Aims and objective

The primary objective of this work will be to investigate ferroelectric semiconductors, p-block compounds, and heterostructures, which are regarded as a new family of photocatalysts. A built-in internal electric field can serve as an electron-hole separator, thus enhancing photocatalytic activity. The built-in internal electric field not only achieves charge separation, but also constructs spatially separated reduction and oxidation sites. The primary aim of this thesis is to study the crystal and electronic structures of p-block ferroelectric (\(d^{10}\) or \(d^0\)) semiconductors and study their photocatalytic activity. The specific aims of the study have been the following:
• Present a literature review on developments in photocatalysis and specify the gap in photocatalysts throughout photocatalytic history.

• Design and apply band engineering to ferroelectric materials consisting of ferroelectric p-block compounds (d^{10} or d^{0} oxide semiconductors).

• Prepare photocatalysts and characterize the materials by different instruments, devices, and techniques and compare them with computational calculations.

• Evaluate the photocatalytic activity of photocatalysts by the degradation of dye under exposure to light and study the stability and the mechanism.

• Compare these results with previous results.

Some questions that need to be answered in this thesis:

• Does an internal electric field enhance photocatalytic activity?

• Does nanoscale size have an effect on the polarization value of a ferroelectric?

• Does a ferroelectric/semiconductor interface produce band bending?

• Does a ferroelectric produce different sites for reduction/oxidation?

1.6 Overview of thesis

• Chapter 1 explains the principle and mechanism of photocatalysis

• Chapter 2 reviews reports from the literature that are related to the present research.

• Chapter 3 presents details on experimental methods, materials used in the experiments, materials preparation, collection and analysis of data, structural characterization methods, electronic structure characterization methods photocatalytic reactor set-up, photocatalysis evaluation, and density functional theory (DFT).

• Chapter 4 discusses Ag_{10}Si_{4}O_{13}, a ferroelectric photocatalyst with visible-light photooxidation properties.

• Chapter 5 discusses the enhancement of charge separation in nanostructures of a ferroelectric heterogeneous photocatalyst, Bi_{4}(SiO_{4})_{3}/Bi_{2}SiO_{5}.

• Chapter 6 discusses the preparation and study of Bi_{4}Ti_{3}O_{12}.

• Chapter 7 contains the general summary and conclusions.

1.7 References


Chapter 2

Literature review

Introduction

The first successful light-to-fuel conversion was carried out by Fujishima and Honda in 1972, which was based on this photocatalysis technique [1]. This has been considered as the start of photocatalytic history. The first material used as the photocatalyst was TiO$_2$, even though it is not a perfect material for photocatalytic applications due to many limitations. One of these limitations is that TiO$_2$ has a wide band gap at 3.0-3.2 eV. Unfortunately, only 5% of solar light impinging on the earth’s surface can be utilized by TiO$_2$ photocatalyst, whereas the visible spectrum forms 40% of solar light [2-4]. Therefore, great efforts have been made to enhance TiO$_2$ in order to utilize the visible spectrum by either band engineering to modulate the energy band or other methods. Even though TiO$_2$ efficiency under visible light has been improved, it is still challenging to apply in practical applications because the recombination rate of electron-hole pairs is high [5-8]. Moreover, stable semiconductor oxides with visible light activity such as WO$_3$ [9-11] and Bi$_2$O$_3$ [12-14] also have low photocatalytic activity. Semiconductors with visible light activity, in particular, metal-based sulfide semiconductors such as CdS, have high photocatalytic activity and are suitable for hydrogen production. Nevertheless, metal sulfides are not stable over the long term [15-17]. Thus, numerous works have been carried out to find a photocatalyst that fulfills the requirements of practical applications. Recently, it was observed that there is a significant enhancement in photocatalytic activity compared with the activity two decades ago. Applications such as air purifiers and self-cleaning windows that work by photocatalysis are already on the market, but photodegradation and water splitting are still challenging. This literature review presents a survey that highlights the achievements and enhancements of photocatalysts.

2.1 Challenges and opportunities to enhance and explore photocatalysis

Although ongoing great efforts have significantly improved photocatalytic activity by providing large surface area and short pathways for photo-induced charges to reach the surface and also have modified the band structure, existing photocatalysts still do not meet engineering requirements such as stability, non-toxicity, visible-light-activity and low cost. These topics will be briefly covered with a survey on overall strategies for enhancement and exploration of photocatalysis, which is classified into four parts as follows: 1. band gap engineering and visible light sensitization, 2. heterojunction systems, 3. photocatalyst built-in internal electric field, and 4. ferroelectric photocatalysts.

2.1.1 Band structure engineering and visible light sensitization

As part of the enhancement of the photocatalytic activity is increasing visible light activity, in particular, where photocatalyst based semiconductors have a wide band gap (i.e. use ultraviolet (UV) light which is only 5% of the light of the sun). The enhancement of visible light activity is
carried out by modifying the band-gap energy of the semiconductor. Thus, semiconductors with a wide band gap cannot utilize the visible light spectrum. The most stable photocatalysts are semiconductor oxides such as TiO$_2$, ZnO, Nb$_2$O$_5$, etc., but unfortunately, those photocatalysts have wide band gaps which are only efficient under UV-light. Element doping of semiconductors is an effective technique to modify the band gap because it creates impurity levels in the forbidden area between the conduction band (CB) and the valence band (VB), leading to an upshift in the VB or downshift in the CB, as shown in Figure 2-1, thus reducing the band-gap energy.

![Figure 2-1](image)

Figure 2-1 Schematic illustration of achieving visible light activity in TiO2 by doping with metals and non-metals [18].

The most efficient photocatalysis reported is for TiO$_2$ (band-gap energy, $E_g = 3.2$ eV), which is highly efficient towards water splitting and organic pollutant degradation. TiO$_2$ doped with Nitrogen atoms is much more effective with respect to visible light activity because the atomic size is comparable to that of oxygen, and it has low ionization energy and high stability [19]. On the other hand, doping with fluorine does not decrease the band gap. The non-metal element dopants (carbon, phosphorus and sulfur) have shown positive results for visible light activity. Doping with non-metal elements, not only increases visible light activity, but also creates trapping sites within the VB and CB that increase the lifetime of photoinduced charge carriers. It should be noted that the requirements on the doping are very strict with respect to atomic size, and the non-metals elements rarely have an affect on the CB [20]. The density of states calculations (as shown in Figure 2-2) reveal that the substitutions of non-metal elements (N, P, S, C) for O can lead to the mixing of non-metal 2p orbitals with O 2p and induce upward shifting of the VB. Co-doping with non-metals such as N and F in TiO$_2$ leads to higher photocatalytic activity than for N- or F-doping separately, because N-doping narrows the band gap, whereas F promotes charges separation. Moreover, the metal element dopants such as V, Fe, Cr, and Co have been shown to increase the visible light activity of TiO$_2$ as well as enhancing the photocatalytic activity [21]. Theoretical calculations have shown that metal-doping in TiO$_2$ such as with Sn$^{4+}$ can create impurity levels in the lower CB of TiO$_2$ and are considered as electron acceptor levels, whereas V$^{5+}$ is considered as an electron donor level in the upper VB of TiO$_2$, as shown in Figure 2-3.
In addition, the impurity energy levels in the lower CB or upper VB can not only serve to make the semiconductor visible-light-active, but also serve as electron and hole traps. Therefore, metal-doping of TiO$_2$ can enhance the photocatalytic activity under visible light. It should be noted that not all metal doping can enhance the photocatalytic activity because metals can sometimes serve as recombination sites as in the case of Al. In such a way, the other photocatalysis capable semiconductor oxides with wide band gaps (such as ZnO) can also benefit from the same strategy as doped TiO$_2$, but there are some differences in the electronic structure. Manganese-doped ZnO has exhibited enhancement of optical absorption under visible light, and the results show higher photocatalytic activity for photodegrading methylene blue (MB) than undoped-ZnO [22]. In general, element doped semiconductors exhibit a change in photocatalytic activity due to changes in the energy band structure [23]. However, simple metal oxides or binary oxides have energy band structures that are not easy to modify because they can only accommodate limited dopant content. Multi-metal oxides such as Ag$^+$ and Bi$^{3+}$ based compounds have recently become more capable of visible light activity by completely or partially replacing one element by another element.

The electronic configurations containing the cations with $d^{10}$ or $d^{10}s^2$ orbitals can introduce occupied $d$- or $s$-states into the VB, which can hybridize with O $2p$ states to produce up-shift of the valence band maximum (VBM). Whereas, the $s$, $p$ states from metal (M) contribute to down-shifting of the energy level of the conduction band minimum (CBM). For example, in the case of Ag-containing multi-metal oxides, AgMO$_2$ (M = Al, Ga, In), the band structures and the DOS have been calculated by density functional theory (DFT). The CBM is mainly constructed from the Ag 5$s$5$p$ and M $s$,$p$ states, whereas all the VBs consist of the Ag 4$d$ and O 2$p$ states. Hybridization occurs between the Ag 5$s$5$p$ and M $s$,$p$ states at the CBM, which enhances visible light activity. Thus, the band gaps of AgAlO$_2$, AgGaO$_2$, and AgInO$_2$ are changed to 2.95, 2.18, and 1.90 eV, respectively [24]. Similarly, the electronic structure of Ag$_2$MO$_4$ (M = Cr, Mo, W) is shown in Figure 2-4, where visible light activity is exhibited by changing the metal from Mo → W.
Cr, where the band gaps are 3.4, 3.1 and 1.8 eV for Ag$_2$MoO$_4$, Ag$_2$WO$_4$, and Ag$_2$CrO$_4$, respectively [25].

Figure 2-3 The DOS of metal-doped TiO$_2$ and pure TiO$_2$. Black solid lines: total DOS (TDOS), and red solid lines: metal-doped TiO$_2$ with 3d states. The blue dashed line represents the position of the Fermi level [26].
The Bi$^{3+}$ based compounds, in particularly, bismuth oxyhalide (BiOX, X = Cl, Br, I) have demonstrated excellent photocatalytic activity towards pollutant degradation. BiOCl possesses a wide band gap, however, and thus, the band gap has been reduced by partially changing the halogen atoms from Cl → Br → I. In general, the band gap decreases with the electronegativity of halogen elements in compounds (Figure 2-5). Therefore, visible light activity has been achieved, resulting in enhanced photocatalytic activity. For example, BiOCl$_x$Br$_{1-x}$ (0 ≤ x ≤ 1) solid solutions have successfully fabricated by the hydrothermal method, and the band gap has been reduced from 3.39 to 2.78 eV by decreasing the ratio of Cl/Br. The BiOCl$_{0.5}$Br$_{0.5}$ exhibited higher photodegradation efficiency towards rhodamine B (RhB) [27].
The $p$-block cations with a $d^{10}$ electronic structure such as $\text{Bi}_2\text{InNbO}_7$ have been given enhanced photocatalytic activity by completely substituting Ga or Al for In, and the band gaps have been estimated: $\text{Bi}_2\text{InNbO}_7$ (3.01 eV), $\text{Bi}_2\text{AlNbO}_7$ (2.79 eV), $\text{Bi}_2\text{GaNbO}_7$ (2.67 eV) [30]. In general, it is easier to modify the band structures of ternary oxides than binary oxides by doping or complete substitution with various metals. Figure 2-6 shows band-gap values for many photocatalysis compounds. In fact, the $p$-block compounds with a $d^0$ or $d^{10}$ electronic structure have been significantly more attractive for research because they exhibit excellent photocatalytic activity. These compounds possess highly dispersive band structures, since the bands consist of anisotropic $p$ and $sp$ states and the $d$ orbitals, either empty or filled, do not not participate in the band structure. The photogenerated charges thus possess high mobility, compared to partially filled $d$ electronic configurations that have flat conduction bands. Hence, the photocatalytic activity has been significantly enhanced with visible-light-active and unique band structures. New families with the configuration $\text{Bi}_x\text{O}_y\text{X}_z$ (X = Cl, Br, I, $x$, $y$, and $z = 1, 2, 3, \ldots, 31$) were explored as promising photocatalysts, such as $\text{Bi}_{25}\text{O}_{31}\text{Cl}_{10}$ [31] and $\text{Bi}_{25}\text{O}_{31}\text{Br}_{10}$ [32]. The CB of $\text{Bi}_{25}\text{O}_{31}\text{Br}_{10}$ has been measured and calculated by Mott-Schottky experiments and DFT, respectively.
It has been proven that, when the CB is upshifted to a negative value vs. normal hydrogen electrode (NHE), Bi\textsubscript{24}O\textsubscript{31}Br\textsubscript{10} has the capability to photocatalyze H\textsubscript{2} evolution from water under visible light, as shown in Figure 2-7. Modifying Bi\textsubscript{x}O\textsubscript{y}X\textsubscript{z} does not only modulate the band gap, but also can produce a band-gap upshift [34-36]. Bi\textsubscript{2}O:Br has been demonstrated excellent activity than BiOBr to photodegradation of dye molecules. This is because the conduction band became more negatively with increasing Bi content and then the conduction possess ability to reduce oxygen molecular to produce \textbullet O\textsubscript{2}. The Figure 2-8 show that Bi\textsubscript{24}O\textsubscript{31}Cl\textsubscript{10} has much producing of \textbullet O\textsubscript{2} compare with BiOCl whereas Bi\textsubscript{24}O\textsubscript{31}Br\textsubscript{10} has shown capability to produce H\textsubscript{2} for water splitting [37].

Nevertheless, the recombination rate is still high, and there is too much chemical instability to apply it in practical application. Great efforts have been made to increase charge separation and visible light activity by combining two materials, which will be discussed in the following sections.
2.1.2 Enhancement of charge separation and visible light activity in heterojunction systems.

A semiconductor in contact with other semiconductors, or molecules, dyes, and metals, can show enhanced photocatalytic activity compared with each component separately. This system is called a heterojunction structure, which can promote charge separation and better utilization of the solar spectrum. The band bending generated when a semiconductor is in contact with other material causes bending in the energy levels of the VB and CB for the semiconductor. The bending results from the different Fermi levels, and thus, in the contact region, the electrons will redistribute themselves between the two materials until the Fermi levels are aligned at equilibrium. The energy levels for the semiconductor will bend upward or downward depending on the differences in the Fermi level. There are many systems of heterojunction according to the materials combined with semiconductors, which are classified in the following sections.

2.1.2.1 Semiconductor-metal composites

One of the actions to promote photocatalysis is coupling a semiconductor (S) to a metal (M), which results in visible light activity and electron-hole separation. Several reports have shown that noble metals on the nanoscale (e.g. Ag, Pt, Pd, and Au) coupled with a photocatalyst (e.g. TiO₂) can enhance the photocatalytic activity.

Composites such as Au/TiO₂, Ag/TiO₂, Au/ZnO, and Ag/ZnO have shown high photocatalytic performance under visible light despite the wide band gap of the semiconductor [38]. Basically, the phenomenon of localized surface plasmon resonance (LSPR) occurs when metal nanoparticles (NPs) (especially Au and Ag) are illuminated by light with a frequency that matches the natural frequency of the surface electrons, which oscillate to resist the restoring force of positive nuclei, but coherently oscillate in phase with the electromagnetic field of the incident light [39]. The photoinduced hot electrons can be injected from Au into the CB for an n-type semiconductor and hot holes can be injected into the VB for a p-type semiconductor, which thus can promote electron-hole separation and then enhance the visible light activity in the composite. Generally,
the noble metals are mostly used to support a wide range of metal oxides and ternary metal oxides. For example, Ag/BiOCl/Pd plasmonic photocatalysts have shown enhanced photocatalytic performance. The photoinduced hot holes in the Ag nanoparticles under visible light can be injected into the VB of BiOCl. In contrast, Pd works by hole trapping that is photoinduced by BiOCl under UV light. Thus, this material can utilize full spectrum with high charge separation. Although BiOCl possesses a wide band gap, it can work under visible light via plasmonic resonance as well as the reduction/oxidation potentials determined by the positions of the VB and CB of BiOCl. Therefore, there are two phenomena that can support enhancement: the metal/photocatalyst plasmonic effect and the Schottky junction. The plasmonic effect can photogenerate hot charge carriers and inject them into the photocatalyst, whereas the Schottky junction can work as a sink to accept charge carriers from the photocatalyst [40]. Figure 2-8 shows Schematic band diagrams for the mechanisms of the plasmonic effect and the Schottky junction in a composite of an n-type and a p-type semiconductor. Another bismuth oxyhalide, BiOX (X = Cl, Br, I), was also loaded with noble metals (Rh, Pt and Pd) It followed the order Pt > Pd > Rh for UV and Rh > Pt > Pd for visible light irradiation.[41]. The results showed significantly enhanced activity. Similarly, silver-based compounds, Ag@AgBr [42], Ag/Ag2PO4 [43], and M/Ag2PO4 (M = Pt, Pd, Au) [44], also showed increased activity. Indeed, the LSPR is significantly affected by the particle size and shape, and the carrier concentration of nanoparticles. Metal-photocatalyst activity is also affected by many factors such as the work function of the metal Schottky barrier at the interface and the electron affinity of the semiconductor [40].
Figure 2-8 Schematic band diagrams show the mechanisms for the plasmonic effect and the Schottky junction in composites with $n$-type and $p$-type semiconductors [45].

2.1.2.2 Semiconductor-Semiconductor composites
Coupling a semiconductor (S) with another semiconductor (S) can enhance charge separation and also improve the visible light activity if one of them absorbs visible light. As can be seen Figure 2-9, high charge separation is expected because the electrons and holes will be driven in different direction. The electron in the CB of S(A) will be injected into the CB of S(B) which has a lower negative potential, and the hole will be injected from the VB of S(B) into the VB of S(A) which has a lower positive potential. This type of heterojunction is called type I, where two semiconductors are of the same type, for example, $n$-$n$ type or $p$-$p$ type.
Thus, the electrons and holes will be separated. In order to absorb the full light spectrum, a narrow band gap $S(A)$ (such as CdS and C$_3$N$_4$) is combined with a wide band gap $S(B)$ (such as TiO$_2$ and ZnO). Thus, the wide spectrum can be absorbed, and there is higher charge separation compared with each photocatalyst separately. Numerous efforts were previously carried out to enhance the photocatalytic activity of the TiO$_2$-based heterojunction, C$_3$N$_4$/TiO$_2$ [47]. Such heterojunctions have shown higher photocatalytic activity than TiO$_2$, because C$_3$N$_4$ absorbs visible light and has a CB higher than that of TiO$_2$ but possesses a high recombination rate. Therefore, the electrons from C$_3$N$_4$ which are photoexcited from visible light can transfer and migrate to the CB of TiO$_2$, giving this heterojunction enhanced photocatalytic activity. There are many reports on this type of heterojunction based TiO$_2$ such as SnO$_2$/TiO$_2$ [48], or CdS/TiO$_2$ [49]. It should be noticed that the S-S composites must have higher interfacing (overlapping) between S-S to enhance charge separation, especially where the difference in lattice spacing is small between two semiconductors. Therefore, electrons and holes can be injected into another semiconductor rather than recombining. According to the previously reported results that heterostructured photocatalysts containing the same elements should be preferred. For example, heterojunctions with the same elements, such as BiOBr/Bi$_2$O$_3$Bi$_{10}$ (Figure 2-10) and Bi$_{1.6}$Mo$_{0.4}$O$_{6.5}$/Bi$_2$MoO$_6$ [50, 51], or two of the same elements, such as Bi$_2$O$_3$-Bi$_2$WO$_6$, BiOI/BiOBr, and BiOBr/Bi$_2$WO$_6$ [52-54], or one same element [55], such as Bi$_2$S$_3$/BiOBr have demonstrated higher photocatalytic activity compared with a heterojunction containing materials with high mismatch in the band structure and lattice. This is because poor interfacing between two semiconductors leads to ineffective electron transfer pathways. The semiconductor $p$-$n$ junction (type II) has high charge carrier separation compared with type I. In this type, the space charge region (depletion layer) at the interface between the two types of semiconductors exists because the electronsm which are majority carriers in $n$-type semiconductor, diffuse inside the p-type semiconductor leaving positive charges, whereas, on the other side, the holes, which are majority carriers in $p$-type semiconductor, diffuse inside the n-type semiconductor leaving negative charges. The diffusion continues until the Fermi level is aligned for two sides. Thus, the $p$-$n$ junction creates band bending and an internal electric field, which are due to powerful charge separation. The photoinduced electrons under light in the
space charge region will be driven under an electric field to the positive region of the \( n \)-type side. Meanwhile, the photoinduced holes will be driven to the negative region of the \( p \)-type side. The photoinduced electrons migrate to the CB of the \( n \)-type side, whereas the holes migrate to the VB of the \( p \)-type side, and thus this type of heterojunction offers longer charge carrier lifetimes, spatial charge carrier separation, and a wide absorption spectrum. As a result, this type of heterojunction is perfect for practical application. Recently, nanotechnology has offered new strategies to enhance photocatalytic activity. Two-dimensional (2D) nanosheets have been demonstrated to have a large surface-to-volume ratio and can provide good platforms on their surfaces to grow materials with different dimensions (such as 0, 1, and 2D). One-dimensional (1D) nanostructures such as wires, tubes, and belts have recently received considerable attention because they are attractive for photocatalytic application. Compared with other dimensions, the 1D types feature excellent charge transport and large surface area. 1D TiO\(_2\) has been shown to have efficient electron-hole separation because of superior charge transport. Zero-dimensional (0D) CdS sensitized 1D TiO\(_2\) nanotube arrays have synthesised and exhibited high photocatalytic activity [56, 57]. SnS\(_2\)/g-C\(_3\)N\(_4\) nanosheets as 2D/2D heterojunction photocatalysts have demonstrated significant enhancement toward Methylene blue (MO) under visible light, and the photodegradation percentage increased from \( \sim 45.5\% \) and \( \sim 35.4\% \) for C\(_3\)N\(_4\) and SnS\(_2\), respectively, to \( \sim 95.0\% \) for SnS\(_2\)/g-C\(_3\)N\(_4\). In this form, the larger contact area exhibits better charge separation compared with point-to-area as in 0D/2D [58]. Recently, constructing ternary composites can produce multiple pathways and channels to transfer electrons and holes, and thus achieve separation. For example, Au nanoparticle (NP) decorated 2D/2D Bi\(_2\)WO\(_6\)/TiO\(_2\) heterojunctions have demonstrated excellent enhancement of photocatalytic activity. Nevertheless, ternary composites have been considered less interesting because of their expensive preparation and lower stability [59]. Ag-based oxides have high photocatalytic activity. Generally, most Ag-based oxides are responsive in the visible light spectrum, but the main reason why these photocatalysts lose their activity is because they easily undergo photocorrosion (Ag\(^+\) + e\(^-\) → Ag). Recently, reports have shown that Ag-based heterojunctions can decrease the photocorrosion. The photocatalytic activity of AgBr/Ag\(_2\)CO\(_3\) heterojunctions was demonstrated to be higher compared with Ag\(_2\)CO\(_3\) alone and was maintained after 4 recycling runs [60], while Ag\(_2\)O/Ag\(_2\)CO\(_3\) heterostructures have shown very much higher and more stable photocatalytic activity than Ag\(_2\)CO\(_3\) and Ag\(_2\)O, respectively [61]. Interestingly, the built-in electrical potential found in \( p-n \) heterojunctions has more advantages than in \( p-p \) and \( n-n \) heterojunctions because there is more effective charge separation and migration in the presence of the local electric field in the region between the two different types of semiconductors (\( p \)-type and \( n \)-type). Ag\(_2\)O/Bi\(_2\)O\(_3\)CO\(_3\) \( p-n \) heterojunction [62] photocatalysts exhibited higher photocatalytic activity and greater stability than pure Bi\(_2\)O\(_3\)CO\(_3\), Bi\(_2\)S\(_3\)/Bi\(_2\)O\(_3\)CO\(_3\) \( n-n \) heterojunctions [63], and Ag\(_2\)O/Ag\(_2\)CO\(_3\) \( p-p \) heterojunctions [64]. In a \( p \)-type semiconductor, the transfer of electrons from \( n \)-type to \( p \)-type and holes from \( p \)-type to \( n \)-type can generate a space charge region, and therefore, a local electric field is formed between the two types of semiconductors. This electric field can assist in charge separation and thus higher photocatalytic activity [65].
Figure 2-10 Photodegradation Rhodamine B (RhB) of over 75% for BiOBr/Bi$_2$O$_3$Br$_{10}$ is 9.0 times higher than over pure BiOBr or Bi$_2$O$_3$Br$_{10}$ [49].

2.1.2.3 Carbon Nanostructured- Semiconductors

It has been shown in previous reports that carbon nanotubes (CNTs) not only have useful mechanical properties and a large specific surface area, but also unique electronic and optical structures. TiO$_2$-CNT heterojunctions have demonstrated excellent charge separation because the CNT has a large electron-storage capacity to accept electrons from the semiconductor, thus suppressing the recombination rate, as shown in Figure 2-11. In addition, CNT has a large surface area, which provides adsorption capacity toward specific species.

The one-dimensional (1-D) morphology of CNTs as a matrix core/shell architecture leads to enhanced facilitation of electronic transport and results in improved quantum efficiency in photocatalysis. On the other hand, 2D graphene (G), graphene oxide (GO), and reduced graphene oxide (RGO or rGO) have shown excellent physical and chemical properties and are promising materials for photocatalytic activity compared with carbon forms such as 0D fullerenes, 1D nanotubes, and 3D graphite. There is an enormous literature on graphene–semiconductor nanocomposites, and they all have enhanced photocatalytic activity. On the other hand, most silver-based photocatalysts are sensitive to visible light and have high photocatalytic activity, but they are subject to high instability. Thus, much research has been done to suppress the decomposition of silver components by coupling them with different forms of carbon. CNT/Ag$_3$PO$_4$, GO/Ag/AgX (X = Cl, Br), and GO–Ag$_3$PO$_4$ heterojunctions demonstrated higher quantum efficiency toward dye degradation and better stability compared with only silver components [66-68]. Ag/Ag-based photocatalysts could also show some other limitations such as low adherence, while hybrid Ag$_3$PO$_4$/RGO/Ag heterostructured photocatalyst showed excellent
quantum efficiency and better stability than Ag$_3$PO$_4$/RGO or Ag/Ag$_3$PO$_4$ [69-71]. On the other hand, in the case of Bi-based photocatalysis, rGO loaded BiOI photocatalyst exhibited enhanced efficiency with increased loading of rGO [72], and hence, 2D carbon can play an important role in transporting electrons far away from the CB of the photocatalyst and support, thus enhancing charge separation.

0D/2D CdS/Graphene (G) composites have shown excellent quantum efficiency in hydrogen production under visible light [75]. The G serves as efficient electron collector and transporter to reduction sites because of its excellent electron conductivity and unique 2D structure, and it also suppresses the photocorrosion of CdS. Amorphous silver silicates/ultrathin 0D/2D g-C$_3$N$_4$ heterojunction composites have been fabricated, and the enhancement was much higher than for g-C$_3$N$_4$ alone [76], whereas 0D/0D-2D CdS–Pt–G nanocomposites significantly enhanced the production of hydrogen under visible light [77].

### 2.1.3 Dye-sensitization Semiconductor

Dye sensitization, more interestingly, can extend light absorption by utilizing longer wavelengths in the spectrum, thus enhancing the quantum efficiency of a photocatalyst, and in particular, supporting a wide band-gap photocatalyst for either hydrogen production or photodegradation. Basically, previously adsorbed dye on photocatalyst surface results in dye cationic radicals that can be excited by a photon. The dye generates electrons in the lowest unoccupied molecular orbital (LUMO), which can be trapped by the conduction band of the photocatalyst (Figure 2-12) and then react with adsorbed O$_2$ and H$_2$O on the photocatalyst surface to produce radical species or water splitting. For example, because Bi$_{24}$O$_{31}$Cl$_{10}$ and rhodamine B (RhB) are compatible in energy level, the Bi$_{24}$O$_{31}$Cl$_{10}$ shows excellent photocatalytic activity under visible light towards
the degradation of RhB, which is promoted by dye sensitization [31]. The same is true of the RhB–BiOCl system [15] and also rhodamine B with K$_2$Nb$_6$O$_{17}$ [78] and Nb$_2$O$_5$ [79].

![Figure 2-12](image1.png)

**Figure 2-12** The basic principle of dye-sensitized photocatalytic H$_2$ production from water [78].

Generally, dye-sensitization photocatalysts offers the choice of a variety of dyes compared with metal nanoparticles that are loaded on a photocatalyst, and each dye possesses different properties that could be suitable for a photocatalyst. The dye should have a wide absorption spectrum, a higher energy potential (LUMO) than the CB of the photocatalyst, and high affinity between dye and photocatalyst [80-82]. Dye-sensitization photocatalysts are utilized for photodegradation of a wide range of pollutants such as benzyl alcohol, chlorophenol, and phenol [83].

### 2.1.4 Enhancement of charge separation by internal electric field and facets

Recently, bismuth-based layered structures with internal electric field have demonstrated high quantum efficiency for photodegradation of organic pollutants such as bismuth oxyhalides. The visible light activity in these components results from hybridizing O 2p and Bi 6s orbitals in the VB, whereas the empty Bi 6p orbital is the main constituent of the CB [84].

![Figure 2-13](image2.png)

**Figure 2-13** Crystal structure of Bi$_3$O$_2$[BO$_2$(OH)] showing the internal electric field direction [85].
The crystal structures of these components are constructed from anisotropic \([\text{Bi}_2\text{O}_2\text{]}^{2+}\) layers intercalated by \(X^-\) ions \((X = \text{F, Cl, Br, I})\), which generates an internal electric field (IEF) between the layers and thus can enhance charge separation [37, 86]. This IEF is generated between \([\text{Bi}_2\text{O}_2]\) slabs, which have strong covalent bonding with the halogen double slabs which act as a weak interlayer (only van der Waals forces) along the \(c\)-axis.

Spatial charge separation generates different sites for reduction/oxidation and thus suppresses back-reaction of intermediates and electron-hole recombination. The higher photocatalytic activity of \([\text{Bi}_2\text{O}_2\text{]}\text{[BO}_2\text{(OH)}\]) than \([\text{Bi}_2\text{O}_2\text{]}\text{CO}_3\) is because \([\text{Bi}_2\text{O}_2\text{]}\text{[BO}_2\text{(OH)}\]) (Figure 2-13) has an internal electric field (IEF), and its sheet structure has shown higher efficiency than irregular structures even though they have a higher specific surface area [85].

![Schematic illustration of electric field direction and photocurrent for BiOCl (BOC-001) and BiOCl (BOC-010) samples](image)

Figure 2-14 Schematic illustration of electric field direction and photocurrent for BiOCl (BOC-001) and BiOCl (BOC-010) samples [87].

Recently, it has been proved that facets affect the photocatalytic activity, depending on the photocatalyst surface. It has been demonstrated that the surface atomic configuration due to different facets leads different photocatalytic activities. By controlling the exposed facets of BiOCl single crystals with different IEF directions, the different photocatalytic activity of the (001) and (010) planes could be demonstrated. The photocatalytic activity of (001) facets benefited from higher charge separation, as illustrated in Figures 2-14 and 2-15. The IEF long (001) facet favours charge separation and short diffusion distances of charge carriers to the surface [87]. In another example, anatase \(\text{TiO}_2\) with \{001\} facets exhibited a more highly reactive surface than with \{101\} facet because \(\text{TiO}_2\) with \{001\} facets has higher surface energy [88]. This is also true of Ag-based photocatalysts, for example, \(\text{Ag}_3\text{PO}_4\) with \{011\} facets exhibited higher quantum efficiency compared with \{100\} facets due to their higher surface energy [89]. Similarly, in Bi-based photocatalysts, BiOI with \{110\} facets exhibited much higher photocatalytic activity than with \{001\} facets towards the degradation of bisphenol under visible light [90]. Facet engineering helps researchers to understand the photocatalysis mechanism and follow the charge carrier pathways. In addition, a heterojunction structure with certain facets exposed makes it much easier to study the mechanism of photocatalysis. A certain facet interface in heterojunctions can serve to promote higher charge separation compared with a disordered interface. In addition, the particular facet interface can make it easy study the mechanism involved, because otherwise the heterojunctions exhibit much complexity in their mechanisms. Recently, other facet heterojunctions have been widely reported and promoted the study photocatalytic behaviour at...
interfaces with different facets. Moreover, electric fields built into composites have demonstrated different activity. For example, g-C_{3}N_{4}/BiOCl (ng-CN/BOC) heterostructures have exhibited different photocatalytic activity depending on the IEF direction.

![Figure 2-15 Photodegradation of bisphenol under visible light by BiOI with (110) and (001) facets [90].](image)

Figure 2-15 Photodegradation of bisphenol under visible light by BiOI with (110) and (001) facets [90].

![Figure 2-16 Schematic illustration of the mechanism of ng-CN/BOC [91].](image)

Figure 2-16 Schematic illustration of the mechanism of ng-CN/BOC [91].

The separation of electrons and holes is more efficient with an in-plane internal electric than an out-of-plane. CN/BOC-010 composites demonstrate more highly efficient activity than CN/BOC-001 composites (Figure 2-16). The IEF of bismuth oxyhalide is not sufficient to separate charges, however, although theoretical calculations suggested that the IEF of C-doped Bi_{3}O_{4}Cl could be magnified by many times. It was experimentally proven that C-doped Bi_{3}O_{4}Cl showed an increased IEF 126 times greater than that of pure Bi_{3}O_{4}Cl (Figure 2-17), and the enhancement in charge separation efficiency was 80% [92]. Also, the adsorption can demonstrate different activity. Exposed facets with a high percentage of oxygen termination show high activity towards H^{+} under acidic conditions. BiOCl with (001) facets showed higher adsorption activity compared with the (110) surface due to the high percentage of oxygen termination.
Employing crystal facet engineering to design hybrid single crystal semiconductor-semiconductor sheets is an important way to enhance photocatalytic activity. It has been confirmed that BiOI(001)/BiOCl(010) has higher activity than BiOI(001)/BiOCl(001) due to low mismatch of the lattice parameters, thus facilitating electron transfer pathway. The facet adjustment of each semiconductor in heterojunction could produce more benefit for maximize the photocatalytic performance. Although this system is very complexity to synthesis, some facet-controlled heterojunctions were prepared, the interfacing with certain facet for each photocatalyst is not main difficultly but also band structure. Band alignment at interfacing can influence on charge transfer, for example, in Cu$_2$O, the face {001} is much higher work function than {111}. Therefore, the electrons and holes will be accumulated at {001} and {111} respectively. Deposited Pd on Cu$_2$O {111} is not useful because Cu$_2$O {111} work function is lower than Pd whereas Cu$_2$O {001} is higher than Pd, therefore, Pd can be used as hole trapping for Cu$_2$O {001}.

2.1.5 Ferroelectric photocatalyst

Photocatalysis based on built-in spontaneous electric polarization that is provided by ferroelectric materials was proposed to promote spatial charge separation, which provides a driving force to move electrons and holes in opposite directions, forming two types of sites, one for reduction and the other for oxidation. Therefore, a photocatalyst with built in spontaneous electric polarization features suppressed charge recombination and drawback reaction. Also, similar behaviour to ferroelectric occurs in pyroelectric, piezoelectric, semiconducting, and electrooptic materials.

The ferroelectric materials have spontaneous polarization arising from the non-centro-symmetric nature of the crystal structure, meaning that the crystal structure is non-zero neutral because the positive and negative charges have non-symmetric positions. This polarization is stable and permanent over a wide range of cruel thermal and chemical environments. The polarization
direction is reversible by an external electric field, causing rearrangement of ions in the crystal structure. Figure 2-18 shows the crystal structure of BaTiO$_3$ under different conditions[91].

![Cubic phase](image)

**Figure 2-18** Schematic illustrations of the BaTiO$_3$ crystal structure show (A) cubic phase at high temperature (above the Curie temperature), while (B) and (C) show displacement of the Ti atom when poling up and down [91].

In ferroelectric materials, some regions are oriented in a certain polarization (i.e. certain atoms or ions in the crystal have the same distortion direction), and other regions are differently oriented. Regions with like polarization are called domains, and the boundaries between them are called domains walls, while c- and c+ domain refers to negative and positive potentials, respectively. These domains have opposite polarization directions, and thus, the polarization can be depleted, which is called depolarization [95]. It has been proven that polarization can have an effect on the photoinduced charges in a photovoltaic solar cell, which tends to promote charge separation [96-104]. In addition, the photoelectrochemical performance is also affected by polarization materials [105-109]. Beside strong charge separation, ferroelectric materials have a high adsorption efficiency due to polar behaviour.

Hybrid ferroelectric semiconductors have a considerable effect on photocatalytic activity. The photovoltaic effect in a ferroelectric significantly enhances charge separation, which sometimes exceeds the band gap. Spatial charge separation has been clearly observed on the surface of ferroelectric BaTiO$_3$. PbO$_2$ and Ag$^{+}$ have been photodeposited on the selected surfaces where the domain orientation has a positive or negative end, and thus, Ag$^{+}$ cations are reduced to Ag on BaTiO$_3$ where the domain is positive and Pb$^{+}$ cations are oxidized to PbO$_2$ on BaTiO$_3$ where the domain is negative[110]. The efficiency increased by a factor of 7.4 when the polarization of K$_{0.5}$Na$_{0.5}$NbO$_3$ via solid solution K$_x$Na$_{1-x}$NbO$_3$ was increased [111]. The enhanced polarization of tetragonal BaTiO$_3$ (non-ferroelectric) with respect to cubic BaTiO$_3$ (ferroelectric) results in enhanced photocatalytic activity. It was confirmed that the reason behind the enhancement of activity is polarization, which is known to promote charge separation [112]. An interfacing semiconductor-ferroelectric/ semiconductor, for example, Ag$_2$O–BaTiO$_3$, was previously studied, and the polarization was maximized by applying ultrasonic waves. As a result, the performance efficiency was significantly enhanced. Separated redox sites have been confirmed for single domain PbTiO$_3$ nanoplates: the upper side is the location for reduction, where electrons are attracted by the positive polarization, and the bottom side is the location for oxidation, where the holes are attracted to the negative polarization. Thus, PbTiO$_3$ has shown selective photodeposition for Pt and MnO$_x$ (Figure 2-19), and the results demonstrated that selectively photodeposited Pt
features much higher performance in hydrogen production compared with random Pt deposition [113]. The $p$-type semiconductor BiFeO$_3$ is considered a promising photocatalyst because its narrow band gap (~2.4 eV) and ferroelectric properties, while BiFeO$_3$ photoelectrode demonstrated that higher photocurrent density was observed in downward polarization (photoelectrode/electrolyte interface) than upward polarization, indicating that the polarization direction at the contact with electrolyte has a considerable effect on the photoactivity [105].

According to the piezo-phototronic effect, the piezoelectric materials could also behave as ferroelectric materials and promote charge separation, except that the piezoelectric materials are activated by external stress such as ultrasound waves or thermal stress. A ZnO-based piezoelectric has exhibited efficient charge separation on applying external strain. Significant enhancement of dye degradation was achieved by the piezoelectric photocatalysts Ag$_2$O/ZnO [114], CuS/ZnO [115], and TiO$_2$/ZnO [116] on applying light and ultrasound waves. Figure 2-20 illustrates the mechanism of the effect of polarization on charge separation, where the electrons of Ag$_2$O have been attracted to the positive potential side of BaTiO$_3$, whereas the holes have been attracted to the negative side of BaTiO$_3$, leading to electron-hole pair separation. Replacing some I$^{5+}$ by V$^{5+}$ in IO$_3$ significantly increases the polarization of ferroelectric BiOIO$_3$, which leads to higher charge separation (Figure 2-21). The enhancement of photocatalytic performance in V-doped BiOIO$_3$ was 10.1 and 21.1 times that of undoped BiOIO$_3$ under visible and UV light. Ferroelectric photocatalysts based on oxide perovskites (ABO$_3$) are mostly wide-band-gap and have low charge mobility [117-119]. Similarly, layered structures with spontaneous polarization such as Bi$_3$O$_2$X (X = SiO$_3$, GeO$_3$) also shows high photocatalytic activity under UV-visible light. The crystal structure consists a single layer of silicate (or GeO$_3$) sandwiched between bismuth oxide layers. Distortion is observed in the silicate chain (c-axis), which is twisted by an angle, and consequently, the Bi ions are slightly distorted, inducing spontaneous polarization perpendicular to the silicate chain, and thus, 2D polarization (out-of-plane and in-plane polarization) has been observed, so it is expected that the charge separation is higher in this kind of material.
Figure 2-20 Schematic diagram (a) showing random movement of photoinduced electron-hole pair; (b) arrangement of photoinduced electron-hole pairs, with the electrons attracted to the positive surface of BaTiO$_3$, whereas the holes are attracted to the negative surface of BaTiO$_3$ [120].

Figure 2-21 (a and b) Photodegradation of RhB by BOIO$_3$ samples under visible and UV light, respectively; (c) Transient photocurrent and (d) photovoltage spectra for V-doped BiOIO$_3$ and BiOIO$_3$ [121].

According to theoretical studies, the CB of bismuth silicate is mainly composed of O 2p and Bi 6s orbitals, whereas the top of the valence band consists of Si 3p and O 2p. Consequently, the sp/p electronic structure means that there is a highly dispersive band structure, leading to high mobility carriers that facilitate charge transfer to the surface faster than the relaxation time or recombination time [122]. On the other hand, Ag-based oxides, such as Ag$_3$PO$_4$ [123-126], Ag$_x$O,
and AgCO$_3$ [127-129], have excellent visible light activity with a highly dispersive band structure similar to those of bismuth oxyhalides. Nevertheless, this photocatalyst has low quantum efficiency. Previous reports have shown that Ag-based silicates have their own internal electric field, such as in the case of Ag$_6$Si$_2$O$_7$ and Ag$_9$(SiO$_4$)$_2$NO$_3$, which have been demonstrated excellent photocatalytic activity, as shown in Figure 2-22 [130].

![Figure 2-22 Schematic diagram of the crystal structure of Ag$_9$(SiO$_4$)$_2$NO$_3$. E is the internal electric field caused by the polar crystal structure [130].](image)

### 2.2 Summary and opportunities

The back-reaction of intermediates, a wide band gap and high rate recombination at the surface of the photocatalyst are major drawbacks to facet photocatalysis. Decreasing the particle size is of limited help, and the recombination rate will be made to increase, as well the band gap, by quantum confinement. Heterojunctions (including p-n junctions or phase junctions) have attracted wide attention due to their ability to absorb a wider spectrum and improve the charge separation. Heterojunctions still have low efficiency, however, because the separation process occurs only in the interface and near interface regions, and also, the enhancement is not high, according to review [83] (except for facet-selective photodeposition [84]). Despite the great efforts previously made to enhance the photocatalytic activity of these photocatalysts to fulfil the requirements of practical applications, it is still low. Therefore, to overcome this issue, strategies were adopted in this work based on the design and engineering of materials with internal electric field properties, such as p-block materials with ferroelectric polarization or p-block materials with heterojunctions providing built-in internal electric fields.

### 2.3 References


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Chapter 3

Experimental techniques

This chapter presents details about materials and instruments that were used in this project, along with a discussion of the advanced techniques used to evaluate the photocatalyst. These instruments used in this project are located in the Institute for Superconducting and Electronic materials (ISEM), the Electron Microscopy Centre (EMC), and the Intelligent Polymer Research Institute (IPRI) in the University of Wollongong (Australia), and also the Department of Physics and Key Laboratory of Micro-nano Measurement, Manipulation and Physics, Ministry of Education (MOE), Beihang University, Beijing (China).

3.1 Materials:
Table 3-1 all the general chemicals and reagents used in this work.

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Table 3-2 all the dyes used in this work.

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<td>C₁₄H₁₄N₃NaO₃S</td>
<td>327.33</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Methylene Blue (MB)</td>
<td>C₁₆H₁₈ClN₃S</td>
<td>319.851</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Pollutants components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular formula</th>
<th>Molecular Weight (g. mol⁻¹)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>C₆H₆O</td>
<td>94.11</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

3.2 Synthesis

The synthesis of all the photocatalysts in this work was conducted by three different methods, the details of which are below:

3.2.1 Solid ion-exchange method

Normally, two precursors that need to react should be dissolved in solution (water or some organic solution) and the ions exchanges between the two materials are produced precipitating non-soluble materials from the solution, which should be crystallized. In some special cases, it is hard to produce crystalline materials by this method, such as in the case of silver silicate compounds, and solid state reaction under high oxygen pressure is very expensive [1]. Thus, it is more attractive to mix the precursors in mortar and press the mixture into pellets at high pressure, and then the ion exchange will proceed at a specific temperature and over a specific time without solvents [2, 3]. The product is then washed several times with water and ethanol to remove residual materials. For more details, see Chapter 4. This method was used to prepare Ag₁₀Si₄O₁₃.

3.2.2 Hydrothermal Method

One of the most popular methods to synthesize uniform nanomaterials with high crystallinity is the hydrothermal method. Control of the morphology of materials, in particular, for application in photocatalysis, to produce nanoparticles, nanosheets, nanowires, etc., can be accomplished by the hydrothermal method [3, 4]. This method is a typical wet-chemical procedure. In this method, the reactant should be soluble in solvents such as water or any organic solvent under base or acidic environmental conditions. At high temperatures and pressures, the dissolved materials start to react, nucleation and crystal growth results in the formation of new materials [4]. In the basic procedure, the dissolved materials after mixing by stirring are poured into Teflon-lined stainless steel autoclaves, sealed, and then heated in an oven at a certain temperature and for a certain time.
and the mixtures is allowed to cool to room temperature. The precipitate is washed several times with distilled water and ethanol to remove residual materials. The advantage of this method is that thin nanosheets of layered structure materials can be prepared which are difficult to prepare by any other method, and it is also possible to prepare heterojunctions and to dope materials. The preparation details are reported in Chapter 5. This method was used to prepare Bi\textsubscript{2}SiO\textsubscript{5}/Bi\textsubscript{4}Si\textsubscript{3}O\textsubscript{12}.

3.2.3 Molten salt synthesis

Molten salt synthesis is one of the most common methods to prepare complex oxide materials such as ceramic materials; this method features enhanced rates of solid state reaction and lower temperature reaction. It is considered that molten salts are good solvents at high temperature. There are a variety of melting temperatures, and different salts can also be mixed to get an appropriate melting temperature. Basically, by this method, the reactants and salts are mixed in a mortar and then heated in furnace to the appropriate molten salt temperature. At this temperature, the mixture start to react, leading to nucleation and crystal growth. It is possible to prepare nanostructures with controllable shapes and sizes, and to prepare large amounts by controlling the temperature, time, and cooling rate as well as solubility of salts [5, 6]. Due to these advantages, this method was used in this work to prepare thin plates of ternary oxides, which is difficult to synthesize by conventional methods. These ternary oxides are especially important for preparing ferroelectric materials which need high temperature[7]. The synthesis of these oxides in different morphologies, and nanoplates in particular, is possible by this method [8]. Herein, preparation details are reported in Chapter 6. This method was used to prepare Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}.

3.2.4 Thin film synthesis

There are many methods to prepare thin film. Thin film synthesis is important for studying the electrochemical properties of a photocatalyst. In this project, the thin film was prepared via the dip-coating method on indium tin oxide (ITO) or fluorine doped tin oxide (FTO) and had an area of 1 cm\textsuperscript{2}. The substrates should be previously cleaned with ethanol under sonication for 10 min. The powder was mixed with binder material (such as PVA) and drop it on substrate drop by drop by pipette and then dried at a specific temperature and for a given time, which provided mechanical stability.

3.3 Characterization: Equipment, instruments, and tools

3.3.1 Scanning electron microscopy / Energy dispersive X-ray spectroscopy

The morphology and material compositions of the samples were investigated and confirmed by the field emission scanning electron microscopy / energy dispersive X-ray spectroscopy (FESEM/EDS). The sample surface is scanned by an electron beam generated by the electron gun at the top of column, and the electron beam is vertically focused on a small area of the sample surface by a magnetic lens. The column is kept under vacuum, and a high acceleration voltage is used to avoid scattering electrons. The electron beam generates secondary electrons after colliding with the sample surface. These secondary electrons are detected by an electron detector. The elements in the sample are also detected by X-rays emitted from the sample surface, which can be measured by an energy-dispersive spectrometer. The SEM produces high resolution images and
very fine details within an area less than 2 nm². In this work, the FESEM (JEOL-7500) was used throughout the project (5 kV, 10 μA, 8 mm work distance). Before testing, the powdered photocatalyst was sprayed on carbon tape, which was previously covered. The tape is put in an SEM holder, and then air is blown to get a uniform dispersion of particles. Finally, the surface is coated with a 15 nm layer of Pt to make the powder surface conducting. The magnifications were different, depending on sample size. For EDS measurements, the settings were different. The accelerating voltage was 20 kV with the maximum emission current 20 μA and the work distance 10 mm. Many points on each sample surface were measured or mapping scanning of surface.

3.3.2 Transmission electron microscopy (TEM)/EDS

The TEM is a microscope with powerful magnification that uses an electron beam accelerated by 300 kV, which can be transmitted through nanomaterials. The parts of a TEM are similar to those of an SEM, but the principle of the TEM is different. In the TEM, the electron beam is transmitted through the sample, which should be nanoscale in size and suspended on a Cu mesh grid. Images are collected after the electrons have been transmitted through the sample. These images are magnified after detection on a fluorescent screen. The TEM images and selected area electron diffraction (SAED) patterns were obtained using a JEOL ARM-200F. The samples were first dispersed in absolute ethanol by a sonication instrument for 10 min, and then one or two drops were dropped on the Cu mesh grid. Finally, the TEM grid was dried in the air for one hour or more.

3.3.3 X-ray powder diffraction

X-ray diffraction (XRD) is a technique that is used to characterize the crystal structure and phase purity of samples. Mainly, the XRD diffractometer consists of three important parts: an X-ray tube, a sample holder, and an X-ray detector. The X-ray tube generates monochromatic X-rays with wavelength λ, which are focused on the sample surface. The interaction between the surface and the monochromatic X-rays should produce constructive interference. The constructive interference follows Bragg’s Law \( n \lambda = 2d \sin \theta \), where \( \theta \) is the diffraction angle and \( d \) is the spacing of a set of lattice planes. The intensity of the diffracted rays is detected by the X-ray detector, and the scanning angles vs. intensity provide crystallographic information. The data are analysed by matching the data with data base that was collected before for many compounds. In this work, XRD were carried out by X-ray diffraction (GBC MMA XRD) with the Cu Kα wavelength of 1.542 Å and at 40 kV, 25 mA. The scan rate and range of angles were 1 deg/s and 10° to 60° respectively.

3.3.4 Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) Spectrophotometer

The basic principle of this instrument is that light (covering a wide range from 100 to 1500 nm) passes through a sample (which may be gas, liquid, or solid). The light intensity is analysed with a monochromator and then detected by a photodetector after passing through the sample. The absorptivity coefficients follow the Beer-Lambert law which is a proportional relationship between the absorbance and the concentration of the sample. The solid powder was measured according to principle of light beam interaction with a smooth sample, and the reflected light was collected in a
hemisphere shaped collector and then analysed.

Figure 3-1  Photograph of UV-Vix_NIR spectrometer and schematic diagram showing the geometry in an integrating sphere.

In this work, a Shimadzu-3600 was used to measure diffuse reflectance spectra (DRS) of the photocatalyst powder by adding an integrating sphere attachment (ISR-3100) to the instrument, as shown in Figure 3.1, with BaSO4 providing a background between 200 nm and 800 nm. The dye concentration in water after photodegradation was also measured by monitoring the peak absorption of dye. The cuvette cell (4 ml in volume and optical path of 1 cm) was used to measure the dye absorption in the range of 300-800 nm, and the reference cuvette cell was filled with pure water for the background of the dye solution. In the case of phenol, it was used to measure absorption in the range of 200-300 nm.

3.3.5 X-ray photoelectron spectroscopy (XPS)

Highly sensitive quantitative information on the elemental composition of a surface target was detected by the XPS technique. The surface target is excited with X-rays, and then photon-electron interaction occurs, with complete or partial photon energy transfer to core electrons. If this energy is sufficient, then an electron is emitted from the sample surface with a given kinetic energy (K.E.). This energy corresponds to the binding energy (B.E.) of the electron in an atom. The electron detector measures the binding energy of the photoelectrons that are emitted from the target under ultra-high vacuum (pressure, \( P < 10^{-9} \) millibar), and therefore, each peak position reflecting a given binding energy of electrons corresponds to the electronic and oxidation state of an element. The binding energy of the core electrons are affected by the electrons bonded with surrounding atoms, and then a chemical shift occurs, which provides information on chemical states. Besides this, the binding energy provides information about the band structure in heterojunctions because the core electrons are affected by surrounding atoms which have different electronegativity. In this work, XPS (PHI660) was performed using a monochromatic Mg Kα X-ray source.

3.3.6 Atomic force microscopy (AFM) and piezoresponse force microscopy (PFM)

AFM is one of the most advanced instruments to measure the 3D topography of a sample with
ultra-high resolution. Nanoscale areas with 40-50 individual atoms can be studied by AFM to determine their crystallographic properties, and it can be used for microscale observations, or even larger than 100 µm, to show living cells. The basic principle is depends on two parts: a mechanical part and an electrical part. A sharp probe maps the height of a surface sample with very close contact to provide information on 3D topography. The movement of the sample is controlled by piezoelectric materials. The vertical vibration of the probe on the surface sample is recorded by a laser beam reflected from the probe surface, and then the laser beam is detected by a quadruple photodiode. The digital signal recorded by the photodiode is analysed by controller and the displayed on a computer [9]. The advantages of AFM are that samples do not need to be prepared and can be observed under ambient atmosphere. AFM is also a low cost instrument compared with SEM and TEM. In this work, Asylum Research AFMs were used to test thickness of nanosheets. Piezoresponse force microscopy (PFM) was used for bismuth silicate nanosheets. The PFM can study ferroelectric properties on the nanoscale, including the characteristics of hysteresis loops and the switching of polarization. The basic principle is that voltage is applied on the probe tip and results in the expansion of the sample when it is in contact with the sample surface. There are more specific details reported in Chapter 5.

3.3.7 Polarization measurement

The ferroelectric materials have non-centrosymmetric crystal structures, which generate polarization that can be reoriented by applying an external electric field. The polarization as a function of the electric field was obtained using an Easy Check 300 (aixACCT Systems GmbH) instrument equipped with a Trek 610E high voltage source, which is used for silver silicate.

3.3.8 Photoelectrochemical and electrochemical measurements

When a semiconductor is immersed in electrolyte in the dark, the charge density will be redistributed in the interface region, and then the charges are transferred between the two materials until an equilibrium state is reached. The Fermi level will be repositioned, and thus band bending will be achieved. The region in the interface where this takes place is called the space-charge layer. The relationship between the capacitance at the space charge layer and the external applied voltage (as shown below in the Mott-Schokky equation 3.1) can make it possible for us to obtain the flat band potential and charge density, which are useful parameters to determine the conduction band and valence band positions of the semiconductor [10].

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_D} \left( E - E_{fb} - \frac{k_B T}{q} \right)
\]

Where

- \( C \) is the capacitance of the space charge region,
- \( k_B \) is Boltzmann's constant
- \( T \) is the temperature
- \( q \) is the electronic charge
- \( \varepsilon \) is the dielectric constant of the semiconductor,
\( \varepsilon_0 \) is the permittivity of free space,
\( N_0 \) is the donor density (electron donor concentration for an \( n \)-type semi-conductor or hole acceptor concentration for a \( p \)-type semi-conductor),
\( E \) is the applied potential,
\( E_{FB} \) is the flatband potential.

A standard three-electrode system was adopted in this system, and the photocatalyst films, platinum wire, Ag/AgCl, and 0.1 M Na\(_2\)SO\(_4\) were used as the working electrode, counter electrode, reference electrode, and electrolyte, respectively. The working electrode was prepared via the dip-coating method on indium tin oxide (ITO) and had an area of 1 cm\(^2\) and frequency of 5 kHz. The Mott–Schottky curves were collected with a VSP-300 potentiostat.

In the photocurrent–time response system, a 300 W Xe lamp with a monochromator and a cut-off filter (\( \lambda > 400 \) nm) was used as the light source. The photocurrent as a function of irradiation time under visible light was collected with zero bias.

### 3.3.9 Photoluminescence (PL) spectra

One application of PL is to determine radiative and nonradiative recombination rates which is an important investigation in photocatalysis. The basic principle is that a light beam is incident on a sample and the sample is excited, so that it emits photons in a relaxation process, which equals the energy between two electronic level. The charge separation was investigated by using photoluminescence (PL) spectra, which were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature and with an excitation wavelength of 320 nm.

### 3.3.10 Surface photovoltage (SPV)

SPV is an important technique to obtain band bending, recombination lifetimes, and interfacing states of \( p-n \) junctions, as well as the minority carrier diffusion length of semiconductors and many more characterizations. The SPV technique investigates the potential of a semiconductor surface while excitation light is applied on surface. Usually, SPV is carried out by preparing a thin film of the semiconductor material on conductive electrode and then applying light with a monochromatic wavelength on the surface of the thin film. A Kelvin probe can usually scan the whole surface without contact. The photovoltage can be investigated by detecting photoinduced charges carriers that reach the semiconductor surface before and after it is illuminated with light equal to or higher than the band gap [11].

### 3.4 Photocatalytic activity evaluation

The photocatalytic activity was evaluated by the decolouration of dyes and photodegradation of phenol, which were used as model organic pollutants in the photocatalytic degradation experiment at room temperature. A 300 W Xe lamp was used as the simulated light source for studying the photocatalytic performance. In a typical process, 50 mL of RhB (10 mg l\(^{-1}\)) (for phenol 20 mg l\(^{-1}\)) and 0.05 g of the as-prepared sample were added together in a 100 mL beaker with a diameter of 6 cm. The suspension was magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium, and then the mixture was irradiated with the light source. At certain time intervals, a 3 mL aliquot was taken and centrifuged to remove the photocatalyst. The
photodegradation activity was analysed using the UV-Vis spectrophotometer by recording the variation of the peak absorption of dyes and phenol.

3.4.1 Determine reaction kinetics $k_t$ and quantum efficiency

To calculate the reaction kinetics $k_t$ of dyes and phenol degradation, the pseudofirst-order kinetic model was derived, as shown in the equation below.

$$K_t = \frac{\ln C_0}{\ln C_t} \quad 3-1$$

Where $k$ is removal rate constant, $C_0$ is the initial dye concentration, and $C_t$ is dye concentration at time $t$ after the start of the photocatalysis process.

The apparent quantum efficiency ($\varphi$) can be expressed as following equation:

$$\varphi = \frac{\text{No. of molecules undergo photodegradation}}{\text{No. of photons accident inside reaction}} \times 100 \quad 3-2$$

3.5 Programs: analysis

The programs were used in this work are listed below in Table 3.3 along with their purpose.

Table 3-3 Programs used in this work.

<table>
<thead>
<tr>
<th>Program name</th>
<th>Ver.</th>
<th>Purpose</th>
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<tbody>
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<td>VESTA</td>
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</tr>
<tr>
<td>Origin</td>
<td>OriginPro</td>
<td>Data analysis and graphing</td>
</tr>
<tr>
<td>Gatan Digital Micrograph</td>
<td>2.11.1404.0</td>
<td>Visualization and analysis of TEM and SAED images, and determining the $d$ spacing value and exposed facet of crystals</td>
</tr>
<tr>
<td>Match</td>
<td>2.3.2</td>
<td>Identify one or more phases of materials and crystal structure from diffraction data.</td>
</tr>
<tr>
<td>NSS</td>
<td>3.3</td>
<td>Analyze the EDS spectrum to find the composition of a sample</td>
</tr>
<tr>
<td>Casa</td>
<td>ver. 2.3.16dev85</td>
<td>XPS analysis</td>
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</table>

3.6 Theoretical calculations

Theoretical calculations have become essential to support experimental results and directly find properties of any solid. It has recently become widespread in the study of the chemical and physical properties of materials for the interpretation and prediction of any solid containing multiple electrons. The band structure, density of states, and polarization for many materials can
be calculated theoretically. It is thus possible to find better materials for batteries, solar cells, photocatalysts, and many other applications. The electronic structure is achieved by solving quantum mechanical equations for a many-electron system. Density functional theory (DFT) is a computational method to solve many-electron systems. This calculation is not very accurate, however, and sometimes not consistent with experimental results. To overcome this source of error, many approximations for the exchange-correlation energy are used to improve the results. Usually, the calculation is obtained using a supercomputer and appropriate software programs. There are several separate programs that are used in calculations such as Vienna Ab-initio Simulation Package (VASP).

3.7 References

Chapter 4

A ferroelectric photocatalyst $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ with visible-light photooxidation properties

4.1 Introduction

Photocatalysis is one of the most promising ways to solve the energy crisis and environmental pollution issues by using solar energy [1-11]. A number of photocatalysts have been proposed and prepared using materials design and band engineering techniques. Some have achieved excellent photocatalytic performance in either water splitting or the elimination of organic pollution. Nevertheless, most of the high-performance photocatalysts proposed so far are transition metal oxide (TMO) based materials. Generally, TMOs have wide band gaps (> 3.0 eV) due to partially filled d-orbitals [12-15] which limits the absorption of visible light. In addition, their valence bands (VBs) and conduction bands (CBs) are less dispersive due to the isotropic d orbitals of transition metals (TM). The photo-induced charge carriers are hence given a large effective mass, which hinders charge separation and mobility, and results in low quantum conversion efficiency in photocatalysis, especially in the visible light spectrum. Consequently, their visible-light photocatalytic performances are not as high as desired. Therefore, the exploration and development of new visible-light responsive photocatalysts with high quantum conversion efficiency through materials design and band engineering have emerged as an urgent and challenging task in the field of photocatalysis.

Recently, AgO-based compounds have been reported with excellent visible-light-driven photocatalytic activities [16-24]. Because of their unique electronic configurations. Since the d orbitals of Ag are fully filled, the p orbitals in these compounds play an important role in the energy levels and dispersion of the VB and CB. Generally, p orbitals lift the top of the VB and/or lower the bottom of the CB in AgO-based photocatalysts, and promote generation of photo-induced electrons and holes under visible light. Moreover, highly dispersive VBs or CBs can be formed due to anisotropic p or hybridized sp states. As a result, the effective mass of photo-induced charge carriers is much smaller in AgO-based compounds, which facilitates charge transfer in the photocatalytic process under visible-light irradiation [25, 26]. Nevertheless, the narrow band gap and dispersive electronic structure also facilitate the recombination of electrons and holes in the photocatalytic process and, in turn, would limit the photocatalytic activities of these compounds. Therefore, AgO-based compounds with efficient charge separation in photocatalysis are still desired, although their visible-light photocatalytic performance is much higher than those of the TMOs.

Among these AgO-based compounds, an Ag-incorporated $p$-block family, silver silicate ($\text{Ag}_x\text{Si}_y\text{O}_z$),[19, 20, 24] has captured our attention recently. Besides the unique $d^{10}$ state of Ag,
both Si and O in Ag$_{x}$Si$_{y}$O$_{z}$ have typical sp/p electronic configurations, which make the band gap, and the VB and CB in Ag$_{x}$Si$_{y}$O$_{z}$ very likely to conform to the optimum electronic structure for visible-light-driven photocatalysts. In particular, an internal electric field is expected in Ag$_{x}$Si$_{y}$O$_{z}$ compounds, owing to the spontaneous electronic polarization induced by the distorted tetrahedral unit (SiO$_{4}$) arrangement [27-29]. This internal electric field can effectively promote spatial charge separation, which addresses the electron-hole recombination issues that are found in the other AgO-based compounds. Moreover, the strength of the internal electric field can be feasibly modulated by the number of distorted arrangements of SiO$_{4}$ tetrahedral, and enhances the photocatalytic activity of silver silicate. As a consequence, Ag$_{x}$Si$_{y}$O$_{z}$ is regarded as a promising compound family for exploring new visible-light-driven photocatalysts because of this unique crystal and electronic structures. Nevertheless, there have been very few investigations aimed at the design and development of Ag$_{x}$Si$_{y}$O$_{z}$ photocatalysts so far.

In this work, we report a new visible-light-driven silver silicate photocatalyst, Ag$_{10}$Si$_{4}$O$_{13}$, which demonstrates high photocatalytic activity towards the elimination of organics. It was found that the excellent photocatalytic performance of Ag$_{10}$Si$_{4}$O$_{13}$ originates from its anisotropic and highly dispersive band structure due to its p-block electronic configuration. Moreover, Ag$_{10}$Si$_{4}$O$_{13}$ exhibits a large ferroelectric polarization due to very large SiO$_{4}$ chains compare to the other SiO$_{4}$-based ferroelectric. It induces an intrinsic internal electric field in Ag$_{10}$Si$_{4}$O$_{13}$, which further enhances the photocatalytic activity by effective separation of photo-induced charges. Our experimental and theoretical results suggest that silver silicates are promising candidate materials to explore visible-light-active photocatalysts through structural and electronic engineering.

4.2 Experimental section

Sample preparation. In a typical experimental process, AgNO$_{3}$ and Na$_{2}$SiO$_{3}$ (99.9%, Sigma-Aldrich Company) were mixed in a mortar in a molar ratio of 2:1 and then pressed into a disk 1 cm in diameter and 3 mm in thickness. The disk was heated in air at 400 °C for 2 h. After that, the product was washed three times with distilled water and ethanol to remove residual NaNO$_{3}$ and AgNO$_{3}$. The sample was dried at 60 °C for 12 h. For comparison, the photocatalytic activity of N doped TiO$_{2}$ was synthesized according to the original report [2].

4.2.1 Characterizations

The purity and crystallinity of the sample were investigated by X-ray diffraction (XRD, GBC, MMA) using Cu Kα radiation with λ = 1.5418 Å. The sample morphology and elemental analysis were investigated by field emission scanning electron microscopy (FESEM, JEOL-7500). The composition of the samples was examined by energy dispersive spectroscopy (EDS) attached to the FESEM. Transmission electron microscope (TEM) images, High-resolution TEM (HRTEM) and Selected area electron diffraction (SAED) patterns were obtained using a JEOL ARM-200F. X-ray photoelectron spectroscopy (XPS, PHI660) was performed using a monochromatic Mg Kα X-ray source. An ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu-3600) was used to measure diffuse reflectance spectra (DRS) by adding an integrating sphere attachment to the instrument, with BaSO$_{4}$ providing a background between 200 nm and 800 nm. The polarization as
a function of electric field was obtained using an Easy Check 300 (aixACCT Systems GmbH) equipped with a Trek 610E high voltage source. In the photocurrent-time response system, a 300 W Xe lamp with a monochromator and a cut-off filter (λ > 400 nm) was used as the light source. The photocurrent as a function of irradiation time under visible light was collected by a KEITHLEY 2400 source meter. The surface photovoltage (SPV) spectroscopy apparatus is composed of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), and a photovoltaic cell. A 500 W Xe lamp (CHFXQ500W, Global Xenon Lamp Power) and a grating monochromator (Omni-5007, no. 09010, Zolix) provide monochromatic light. The construction of the photocurrent-time-response cell and the photovoltaic cell was in the form of a sandwich-like structure of indium tin oxide (ITO)-sample-ITO. The Mott-Schottky curves were collected with a PARSTAT-2273 Advanced Electrochemical System (Princeton Applied Research). The Ag₁₀Si₄O₁₃ film, Pt foil, SCE, and saturated KCl solution were used as working, counter, and reference electrodes, and as the electrolyte, respectively. The working electrode was prepared via the dip-coating method. The Mott-Schottky measurements were monitored at a fixed frequency of 100 Hz with 10 mV amplitude at various potentials.

Photocatalytic activity measurements. Rhodamine B (RhB), methyl orange (MO), methylene blue (MB), and phenol were used as target organics in photocatalytic degradation tests. All the dyes and the phenol were purchased from Sigma-Aldrich. The photocatalytic activity was carried out at room temperature using Ag₁₀Si₄O₁₃ as photocatalyst. The light source used in the photocatalytic measurements was a 300 W W-Xe lamp with a UV cut-off filter (λ > 420 nm). In a typical process, 100 ml of RhB, MO, or MB solution (10 mg/L for all dyes) and 0.1 g Ag₁₀Si₄O₁₃ were added together in a 250 ml beaker. The suspensions were magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium, and then the mixture was exposed to the light source. The photodegradation of the dye solutions was analysed by UV-Vis spectrophotometer. To stand in for real organic pollutants, phenol was used under the same conditions, but the concentration and volume were 20 mg/L and 50ml respectively. The suspensions were magnetically stirred in the dark for 120 min to reach adsorption-desorption equilibrium, a sample taken every 20 min. For comparison, the photocatalytic activity of N doped TiO₂ was measured under the same conditions.

Theoretical calculations: The calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) based on density functional theory with the projector augmented wave (PAW) pseudopotential method. We applied hybrid functional calculations to simulate ferroelectricity in this work. The short-range exchange potential was calculated by mixing a fraction of nonlocal Hartree–Fock exchange with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE). A conjugate-gradient algorithm was used to relax the ions into their ground states, and the energies and the forces on each ion were converged within 1 ×10⁻⁵ eV/atom and 0.01 eV/Å, respectively. The Koln-Sham orbitals were expanded by a plane wave basis set, and an energy cut-off of 550 eV was used throughout. The Brillouin-zone integration was performed by using the Gamma-centered Monkhorst-Pack scheme with 6 × 4 × 3 k-points.

4.3 Results and discussion
The XRD pattern of the as-prepared sample is shown in Figure 4-1. All the diffraction peaks can be indexed to Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13} with a triclinic structure (space group P-1), according to the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 01-071-1365. The sample consists of phase-pure reddish powders without any observable impurities. In the triclinic structure of Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13}, as illustrated in the inset of Figure 4-1, four tetrahedral SiO\textsubscript{4} units are connected through a corner-shared oxygen atom, forming a distorted Si\textsubscript{4}O\textsubscript{13} chain which is coordinated with the Ag ions.

![XRD pattern](image)

Figure 4-1 XRD pattern of the as-prepared Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13}. The inset is the crystal structure of Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13}.

The FESEM images reveal that the as-prepared Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13} sample consists of micron-sized irregular particles (Figure 4-2). As shown in Figure 4-3 (a) and (b), TEM image, HTEM and the SAED pattern verifies excellent crystallinity of the Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13} sample. HRTEM results (Figure 4-3 (a)) clearly show the lattice fringes of as-prepared Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13} particles with d-spacing of 0.197 and 0.279 nm, which can be assigned to (-104) and (-411) directions of triclinic structure, respectively.
Figure 4-2 SEM image of the as-prepared Ag$_{10}$Si$_4$O$_{13}$

Figure 4-3 Figure 4-3 (a) TEM image and (b) HETEM image and inset SAED pattern of Ag$_{10}$Si$_4$O$_{13}$. 
The elemental composition and chemical states of Ag_{10}Si_{4}O_{13} were further analysed by XPS, as shown in Figure 4-3 (a). The survey spectrum demonstrates that the main peaks correspond to Ag 3d_{5/2} and Ag 3d_{3/2}, O 1s, and Si 2p orbitals for the Ag_{10}Si_{4}O_{13} sample. Detailed spectra providing the fine information for Ag, Si, and O are presented in Figure 4-3 (b), (c) and (d) in which the peaks of Ag 3d_{5/2} and Ag 3d_{3/2} are located at 367 eV and 373 eV, whereas the peaks of Si 2p and O 1s are located at 100.8 eV and 530.6 eV, respectively. The valences of Ag and Si are thus identified as +1 and +4, respectively.

The energy dispersive spectroscopy (EDS) spectrum shows (Figure 4-5) that the atomic percentages of Ag, Si, and O in the sample are 26%, 12%, and 42%, respectively as shown in inset Figure 4-5, which further confirms the composition of phase-pure Ag_{10}Si_{4}O_{13}.
Figure 4-5 shows the diffuse reflectance spectrum of Ag_{10}Si_{4}O_{13} collected by ultraviolet-visible (UV-Vis) spectroscopy. The absorption edge is located at about 700 nm. The band gap ($E_g$) of Ag_{10}Si_{4}O_{13} was then estimated to be 1.72 eV according to the Tauc formula [30], as is shown in the upper right inset of Figure 4-6. It indicates that Ag_{10}Si_{4}O_{13} can absorb almost all the visible-light spectrum. The narrow band gap of the as-prepared Ag_{10}Si_{4}O_{13} sample is believed to have arisen from the hybridization of different orbitals in this Ag-incorporated p-block compound. Thus, density functional theory (DFT) calculations were carried out in order to reveal the electronic structure of Ag_{10}Si_{4}O_{13}. The calculated band structure is shown in Figure 4-7. The band gap is calculated as 1.71 eV, which agrees well with our experimental results based on the photo-absorption edge.

The high symmetry points of the CB and VB are located at the $\Gamma$ and $Z$ points, respectively, giving Ag_{10}Si_{4}O_{13} the features of a typical indirect band-gap semiconductor. It is well known that the excited electrons in an indirect-band-gap semiconductor have a longer lifetime. The separation and migration of photo-induced charge carriers are thus expected to be more efficient. Moreover, a typical signature band structure of the p-block configuration is revealed by our DFT results, in which the CB is highly dispersive whereas the VB shows much less dispersion in Ag_{10}Si_{4}O_{13}.
Figure 4-6 UV-vis diffuse reflectance spectra of Ag$_{10}$Si$_{4}$O$_{13}$. Inset at the top right of (d) is the derivation of the band gap value; Inset at the bottom left of figure is a photograph of the photocatalyst.

Figure 4-7 DFT calculated electronic structure of Ag$_{10}$Si$_{4}$O$_{13}$, in which a dispersive CB and flat VB can be observed.

As shown in Figure 4-8, the CB of Ag$_{10}$Si$_{4}$O$_{13}$ mainly consists of Ag 5s and 5p orbitals. The large amount of hybridization between Ag s and Ag p occurs due to short Ag-Ag bonds. This indicates that the CB is constructed without the “contamination” of less
dispersive d states. As a result, the photo-excited electrons have a small effective mass, which enables photo-excited electrons to easily move to surface active sites due to their high mobility. In contrast, the VB of Ag$_{10}$Si$_4$O$_{13}$ is mainly contributed by Ag 4d orbitals. This leads to a flatter band (as compared to the CB) and thus generates “heavy” holes in the photo-excitation process. This electronic configuration suggests high quantum conversion efficiency for Ag$_{10}$Si$_4$O$_{13}$ under visible light.

Figure 4-8 Partial density of states calculated by DFT.
It is well known that the energy positions of the CB and VB are the primary factors that determine whether the semiconductor can be used in photocatalytic reduction or oxidation. We therefore carried out Mott-Schottky measurements of Ag$_{10}$Si$_4$O$_{13}$, as shown in Figure 4-9. The relative position of the CB edge can be calculated from the empirical equation $E_c = \chi - 0.5 E_g + E_0$, where $E_0$ is a scale factor relating the reference electrode redox level to the absolute vacuum scale ($E_0 = -4.5$ eV for normal hydrogen electrode (NHE)), $E_g$ is the band gap, and $\chi$ is the absolute electronegativity of the semiconductor. The calculated $E_c$ from this equation is empirical and theoretical. Therefore, electrochemical flat-band potential measurements were adopted. The flat-band potential values are obtained by the Mott-Schottky equation [32, 33], as shown in Figure 4-9. The flat potential is calculated to be 0.523 V versus saturated calomel electrode (SCE), which is equivalent to 0.729 V (NHE vs. Ag/AgCl = 0.206 V). It is well accepted that the CB of n-type semiconductors is about -0.1 V higher than the flat potentials, depending on the electron effective mass and carrier concentration. With an applied voltage difference of 0.05 eV between the conduction band and the flat potential, the bottom of the CB is derived as 0.679 eV. The inset in Fig. 2c shows a schematic diagram of the redox potential of Ag$_{10}$Si$_4$O$_{13}$, corresponding to the Mott-Schottky fitting result. The CB and VB edges (inset in Figure 4-9) of Ag$_{10}$Si$_4$O$_{13}$ are +0.679 eV and +2.4 eV vs. NHE, respectively. The lower potential of the VB with respect to the O$_2$/H$_2$O redox potential indicates that Ag$_{10}$Si$_4$O$_{13}$ possesses strong photo-oxidative capabilities and can be used as an oxidative photocatalyst.
In view of the possible strong photo-oxidative capability, the photocatalytic activity of \( \text{Ag}_{10}\text{Si}_4\text{O}_{13} \) was evaluated by the photodegradation of organic compounds, including Rhodamine B (RhB), Methyl orange (MO), methylene blue (MB), and phenol, under visible light irradiation. The results are shown in Figure 4-10 (a), (b) and (c).

![Figure 4-10](image)

Figure 4-10 UV-Visible absorbance spectra for the photodegradation of (a) MO, (b) RhB and (c) MB under visible light over \( \text{Ag}_{10}\text{Si}_4\text{O}_{13} \) recorded after different degradation times. The insets shows the color changes of the (a) MO, (b) RhB and (c) MB solutions corresponding to the five degradation times from 0 min to 40 min.
All the photocatalytic degradation measurements were carried out after the dark reaction, in which the equilibrium adsorption states were reached. The Ag_{10}Si_{4}O_{13} sample exhibits excellent visible-light photocatalytic degradation activity, which is better than that of N doped TiO_2 and the other AgO-based reference samples.

For example, under visible-light irradiation, the absorption peak of MB at 664 nm decreased rapidly with increasing irradiation time and eventually disappeared after 40 min, suggesting excellent photocatalytic performance of the Ag_{10}Si_{4}O_{13} (Figure 4-10 (c)). This demonstrates that the MB can be completely decolourisation by Ag_{10}Si_{4}O_{13} under visible light. The inset in Figure 4-10 shows the visible changes in the color concentration of the MB, RhB and MO solution during the photo-oxidation process. The excellent photocatalytic degradation activities of Ag_{10}Si_{4}O_{13} were also demonstrated with the other dyes, which are shown in Figure 4-10 (a) and (b). By monitoring the signature absorption peaks of RhB, MB, and MO at 556 nm, 664 nm, and 470 nm, respectively, plots of the visible-light degradation ratio versus reaction time were obtained and are shown in Figure 4-11. We note that the complete decolourisation of MB and RhB, and the 80% degradation of MO can be achieved after 30 min, 40 min, and 40 min, respectively. The photocatalytic degradation reaction of the samples followed the pseudo-first-order linear relationship with reaction rate constants (k) as shown in the inset of Figure 4-11.

Figure 4-11 photodegradation rate of organic dyes over Ag_{10}Si_{4}O_{13} under visible light.
Figure 4-12 Cycling runs in the photodegradation of RhB over Ag_{10}Si_{4}O_{13}.

Figure 4-13 Comparison of the photodegradation percentages of Ag_{10}Si_{4}O_{13} and N doped TiO_{2} (N–TiO_{2}) under visible light for different organic dyes.

The photocatalytic stability of Ag_{10}Si_{4}O_{13} in photodegradation was also studied by a photocatalytic cycling test, as shown in Figure 4-12. Ag_{10}Si_{4}O_{13} shows stable photocatalytic
performance for eight photocatalytic degradation cycles. The decreased photocatalytic activity in the first several rounds is due to initial instability of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, which is general for the other Ag-based photocatalysts [34, 35]. It is believed that a small amount of Ag nanoparticles form on the surface of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ at the very beginning photocatalytic cycles. These Ag nanoparticles then function as electron trapping centres to suppress further photocorrosion of the samples, which is evident by stable photocatalytic performance after third run. It should be noted that our $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample shows much higher photo-oxidation activity than the N doped TiO$_2$ reference sample under visible-light, as shown in Figure 4-13, which verifies its excellent visible-light photocatalytic activity towards degradation of organics. We also carried out photocatalytic degradation of colorless phenol over our $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample under visible light irradiation. As shown in Figure 4-14 and Figure 4-15, it is found that the phenol can be completely degraded in 80 min. The inset in Figure 4-14 shows the plots of the rate constants (k) versus reaction time. The above results confirm that the photocatalytic dye degradation activity of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ cannot only be attributed to the dye-sensitization effect because the colorless phenol only absorbs light with wavelengths of 260-280 nm. The k of MB, MO, RhB and phenol are 6, 2.68, 5.7, 2 s$^{-1}$ respectively, as shown in Table (1). The apparent quantum efficiency are 0.78, 0.83, 1.23, 4.4 respectively [36].

Figure 4-14 Photodegradation rate of phenol over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ under visible light. Data points represent an average of duplicate measurements, and error bars represent one standard deviation; the inset shows the kinetic study of the photocatalytic degradation process of phenol under visible light over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. 
The mechanism behind the excellent visible-light photocatalytic activity of our $\text{Ag}_{\text{10}}\text{Si}_{\text{4}}\text{O}_{\text{13}}$ sample was investigated. It is well known that the photocatalytic activity is dominated by several chemical dynamic processes in photocatalysis, including charge excitation, charge separation, and charge transfer. In our photocatalytic degradation measurements, $\text{Ag}_{\text{10}}\text{Si}_{\text{4}}\text{O}_{\text{13}}$ shows superior photocatalytic activity relative to N doped TiO$_2$ and the other Ag-based p-block photocatalysts (Figure 4-16). This indicates that one or several key steps involved in the photocatalytic dynamics under visible light would be promoted by the electronic structure of $\text{Ag}_{\text{10}}\text{Si}_{\text{4}}\text{O}_{\text{13}}$. 

Table 4-1 the $\varphi$ value for different organic pollutants

<table>
<thead>
<tr>
<th>Parameter for photocatalytic degradation with $\text{Ag}<em>{\text{10}}\text{Si}</em>{\text{4}}\text{O}_{\text{13}}$ as photocatalyst</th>
<th>MB</th>
<th>MO</th>
<th>RhB</th>
<th>phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ (s$^{-1}$)</td>
<td>6</td>
<td>2.68</td>
<td>5.7</td>
<td>2</td>
</tr>
<tr>
<td>$C_0^*$ (μmol) × $K$ (s$^{-1}$)</td>
<td>7.5</td>
<td>8</td>
<td>11.8</td>
<td>42.4</td>
</tr>
<tr>
<td>Incident photons (μmol. s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td>958.4</td>
</tr>
<tr>
<td>Apparent quantum efficiency %$^{\scriptscriptstyle*}$</td>
<td>0.78</td>
<td>0.83</td>
<td>1.23</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 1. The apparent quantum efficiency (QE) for different organic components.
Figure 4-16 Photodegradation of phenol within 20 min over different Ag-incorporated p-block photocatalysts. References: Ag$_2$CO$_3$[37], Ag$_3$PO$_4$[38], Ag$_7$Si$_2$O$_7$[24], Ag$_{10}$Si$_4$O$_{13}$ our work.

We carried out photocurrent response measurements of Ag$_{10}$Si$_4$O$_{13}$ under visible light irradiation, as shown in Figure 4-17. It can be seen that the photocurrent generated in Ag$_{10}$Si$_4$O$_{13}$ under visible light is $2 \times 10^{-1} \text{mA/cm}^2$ at the beginning of irradiation, which is higher than that ($1 \times 10^{-1} \text{mA/cm}^2$) of a typical visible-light-driven AgO-based photocatalyst Ag$_3$PO$_4$[39]. The ON-OFF cycles measurement of photocurrent demonstrates that Ag$_{10}$Si$_4$O$_{13}$ possesses high quantum conversion efficiency, and there is a low recombination rate of photo-induced charge carriers under visible-light illumination. It should note that gradually decrease of photocurrent at first three cycles is due to photocorrosion of sample as a result of formation of Ag nanoparticles. We went on to collect surface photovoltage spectra (Figure 4-18) which confirms the high separation rate of photo-induced charge carriers in Ag$_{10}$Si$_4$O$_{13}$, especially in the spectral range from 300 to 600 nm. The efficient separation of photo-induced charges is most likely the key factor contributing to the excellent photocatalytic activity of Ag$_{10}$Si$_4$O$_{13}$, as compared to the other p-block photocatalysts.
Figure 4-17 Photocurrent density response with the light on/off over Ag$_{10}$Si$_4$O$_{13}$.

Figure 4-18 Surface photovoltage spectrum of Ag$_{10}$Si$_4$O$_{13}$, which shows its highest response in the visible-light range.

In fact, the separation of electron-hole pairs in Ag$_{10}$Si$_4$O$_{13}$ would not be expected to be so effective if one only considered its electronic structure. The reasons for the greater efficiency are as follows: Firstly, the charge recombination process also takes advantage of the dispersive band structure in Ag$_{10}$Si$_4$O$_{13}$. The chances for separation and recombination would be traded off in the
photocatalytic process. Secondly, our DFT results reveal that photo-induced holes in Ag_{10}Si_{4}O_{13} possess a large effective mass due to the relatively flat VB. This would be expected to limit the movement of photo-induced holes to surface active sites of Ag_{10}Si_{4}O_{13}, and thereby, limit the photo-oxidative activity of Ag_{10}Si_{4}O_{13}. Nevertheless, this is obviously contradictory to our results on the photocatalytic degradation of dyes and phenol in Figure 4-11. Therefore, it is suspected that the effective separation of photo-induced charge carriers in Ag_{10}Si_{4}O_{13} is caused by another mechanism in addition to the p-block electronic configuration.

In Ag_{x}Si_{y}O_{z} compounds, an internal electric field may exist due to the distorted SiO_{4} tetrahedral chains that are formed in the crystal structure. This internal electric field can overcome charge recombination and promote spatial separation of electrons and holes. Interestingly, Ag_{10}Si_{4}O_{13} has the longest distorted SiO_{4} chains in the Ag_{x}Si_{y}O_{z} family. They most likely induce an internal field due to spontaneous polarization. In order to verify this, a ferroelectric polarization measurement was conducted. As shown in Figure 4-19, we observed the ferroelectric polarization-electric field (P-E) hysteresis loops of Ag_{10}Si_{4}O_{13}, which were obtained through a pulsed positive-up-negative-down (PUND) polarization measurement. A typical unsaturated ferroelectric hysteresis loop with a remanent polarization (Pr) of 0.05 µC/cm^{2} was obtained in electric field of 100 V/cm, as shown in Figure 4-17. This result verifies the existence of an internal electric field in Ag_{10}Si_{4}O_{13} due to an intrinsic electric polarization. Corresponding to the DFT-simulated three-dimensional (3D) charge density distribution (Figure 4-20), the spontaneous electric polarization in Ag_{10}Si_{4}O_{13} is attributed to misaligned positive and negative charge centers in the Ag_{10}Si_{4}O_{13} unit cells, in which O is the charge acceptor and Si is the main charge donor, with little charge decrease for Ag in the crystal. This result suggests that the spontaneous electric polarization in Ag_{10}Si_{4}O_{13} is attributable to misaligned positive and negative charge centers, which are mainly induced by the asymmetrical Si-O tetrahedral chains in Ag_{10}Si_{4}O_{13} unit cells. Given this structure, the calculated spontaneous polarization is about 64.78 µC/cm^{2}, and the polarization direction is indicated in Figure 4-21.

We also find that the O1-O1 bonds in the chains are twisted with angles of 143º and 166.4º (Figure 4-22) accompanied by a coherent displacement of the Ag ions, as well as a distortion of the O3. The SiO_{4} tetrahedra show a spiral distortion with respect to each other on the SiO_{4} chains. The spontaneous polarization along the c direction is induced by the relative displacement of these anionic SiO_{4} tetrahedral units and cationic Ag-O layers. Concurrently, the Ag ions are slightly shifted to a direction normal to the O3, thereby also creating electronic polarization along the a direction. The internal electric field is believed to be the main driving force for charge separation in Ag_{10}Si_{4}O_{13}. Our investigation has demonstrated that the excellent visible-light photocatalytic activity of Ag_{10}Si_{4}O_{13} is attributable to its p-block electronic structure as well as structural distortion, which provides a new strategy to design and develop visible-light-driven photocatalysts to eliminate pollution.
Figure 4-19 P-E hysteresis loop of Ag$_{10}$Si$_4$O$_{13}$ at different applied voltages and frequency 1 kHz.

Figure 4-20 Charge density map; the isosurfaces are 0.01e / Å$^3$ of Ag$_{10}$Si$_4$O$_{13}$. 
4.4 Conclusions

The visible-light-driven photocatalyst Ag_{10}Si_{4}O_{13} was synthesized by the ion-exchange method. It was found that Ag_{10}Si_{4}O_{13} possesses excellent photocatalytic performance towards degradation of dyes and phenol over the entire visible light spectrum. The photocatalytic activity of Ag_{10}Si_{4}O_{13} is attributed to high quantum conversion efficiency because of its narrow band gap,
dispersive band structure, and internal electric field. This unique electronic structure and internal electric field originate from the p-block electronic configuration and distorted SiO$_4$ chains in Ag$_{10}$SiO$_{13}$.

4.5 References

Chapter 5

Enhancement of charge separation in ferroelectric heterogeneous photocatalyst Bi$_4$(SiO$_4$)$_3$/Bi$_2$SiO$_5$ nanostructures

5.1 Introduction

Among several strategies for promoting electron-hole separation, building an electric field internally or band bending in the interface have been proved to be efficient ways to accelerate the electron-hole separation and drive the carriers to the interface for the water splitting reaction or for organic pollutant degradation [1-4]. Recently, the spontaneous polarization in a typical ferroelectric semiconductor has been reported to enhance separation of photogenerated charge carriers at the different facets of the crystal [5-7]. The generation and control of polarization from ferroelectric domains are, therefore, expected to represent a new strategy for designing novel photocatalysts, which may induce electric fields due to energy band bending of similar magnitude to that of p-n junctions.

The silicate-based compounds, as a new ferroelectric materials family, have shown huge potential for photocatalysis due to their high polarization and internal electric field induced by the distorted tetrahedral unit (SiO$_4$) arrangement [8-10]. In our previous work, we showed that the silicate compound Ag$_{10}$Si$_4$O$_{13}$ with silicate chains featuring p-orbital electronic configurations was successfully prepared [11]. The p-block element-based dispersive band structures guaranteed high mobility of the photoinduced carriers [12-15] and the strong internal electric field caused by the distortion of the long silicate chains further accelerated the separation of these electron-hole carriers, resulting in a highly effective photocatalytic performance. As another typical silicate compound featuring p-orbital electronic configurations, Bi$_2$SiO$_5$ was expected to be a superior photocatalyst because it also has highly dispersive band structures and highly ferroelectric polarization. Nevertheless, Bi$_2$SiO$_5$ has been reported to show unsatisfactory photocatalytic activity towards inorganic degradation [16-20]. Similar to other layered Aurivillius-type oxides, Bi$_2$SiO$_5$ is crystallized in layered structures composed of [Bi$_2$O$_2$]$^{2+}$ slabs interleaved with anion layers and tends to expose a crystal plane perpendicular to the c-axis (parallel to the [Bi$_2$O$_2$]$^{2+}$ layer) during the growing process for crystals or nanocrystals [21]. Unfortunately, the main direction of the polarization and internal electric field is along the c-axis for Bi$_2$SiO$_5$ [22, 23]. This means that, for most Bi$_2$SiO$_5$ nanostructures, especially Bi$_2$SiO$_5$ nanosheets, the photoinduced electron-hole pairs could separate under the polarization but would have to travel long distances to reach the active edge sites because of the large length to height ratio of the two-dimensional crystal structure. The separated charges are likely to be trapped by defects along the diffusion path, and the spatial charge separation driven by the polarization could not significantly promote the photocatalytic reaction occurring on the surface of Bi$_2$SiO$_5$.

In this work, we overcome and utilize the intrinsic disadvantage of the polarization direction in bismuth silicate nanosheets for photocatalysis, by constructing unique zero-dimensional – two-
dimensional (0D-2D) Bi₄(SiO₄)₃/Bi₂SiO₅ heterogeneous nanostructures. The heterostructures were successfully synthesized by \textit{in-situ} growth of Bi₄(SiO₄)₃ nanodots on the Bi₂SiO₅ nanosheets via a one-pot hydrothermal process. It is the connection between these two bismuth silicate compounds, and thus, the resultant band bending at the interface, which drives the photogenerated charge carriers in these two semiconductors to the relevant sides [24]. Moreover, a photocatalyst heterostructure build-in the same elements but different phases has been shown significantly enhancement photocatalytic activity [25, 26]. Integrating the internal polarization direction with the heterostructure-induced charge-separation direction, the photoinduced charge carriers in this heterogeneous structure are effectively separated and are driven to the surface rather than to the edge sites, significantly enhancing the photocatalytic performance. The \textit{p}-orbital electronic configurations that are characteristic of both bismuth silicates here guarantee the high mobility of the carriers, which also contributes to the charge separation and photocatalytic performance.

5.2 Experimental

5.2.1 Synthesis of bismuth silicate

All chemicals were analytical grade and used as received from Sigma-Aldrich without further purification. The Bi₄(SiO₄)₃/Bi₂SiO₅ nanosheet (BSO-HNS) 0D-2D heterostructures were synthesized by the hydrothermal method. 0.1 g of cetyltrimethylammonium bromide (CTAB) and 0.1 g of polyvinylpyrrolidone (PVP) (30 K) were pre-dissolved in 5 ml distilled water and then mixed with 0.05 M Bi(NO₃)₃·5H₂O solution. 0.5 mmol Na₂SiO₅ was added to the above mixture under magnetic stirring. The pH value of the solution was then adjusted to 10 by adding NaOH. After stirring for 10 min, the mixture was transferred into a stainless-steel Teflon-lined autoclave with 100 mL capacity. The autoclave was sealed and heated at 200 °C for 6 h and then cooled to room temperature. The collected products were centrifuged, rinsed with distilled water and ethanol, respectively, and then dried at 60 °C for 5 h.

For comparison, our samples with pure phase Bi₂SiO₅ (BSO1) and Bi₄(SiO₄)₃ (BSO2) were synthesized under the same conditions. 1 mmol Bi(NO₃)₃·5H₂O was added into 20 mL mannitol solution (0.1 M) under sonication and stirred for 15 min until the solution became clear. 0.5 mmol Na₂SiO₅ was then added to obtain BSO1 (1 mmol for the synthesis of BSO2). The pH values of the solutions were then adjusted to 10 by adding NaOH. The mixture was transferred into a stainless-steel Teflon-lined autoclave with 100 mL capacity. The autoclave was sealed and heated at 180 °C for 12 h (24 h for BSO2), and then cooled to room temperature naturally. The collected products were centrifuged, rinsed with distilled water and ethanol, respectively, and then dried at 60 °C for 5 h.

5.2.2 Characterizations

The purities and crystal structures of the samples were investigated by X-ray diffraction (XRD, GBC, MMA) using Cu Ka radiation. The sample morphology and elemental analysis were performed by field emission scanning electron microscopy (FESEM, JEOL-7500). The composition of the samples was examined by an energy dispersive spectroscopy (EDS) instrument coupled to the FESEM. The valences of elements were studied by X-ray photoelectron
spectroscopy (XPS, PHI660), which was performed using a monochromatic Cu Kα X-ray source. Morphologies and structures were further examined by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) (JEOL, JEM-2010). An ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu-3600) was used to collect diffuse reflectance spectra (DRS) with an integrating sphere attachment to the instrument, with BaSO₄ providing a background between 200 nm and 800 nm. The on-off photocurrent–time-response (bias voltage = 0 V) and the Mott–Schottky curves were collected with a VSP-300 potentiostat, and a 300 W Xe lamp was used as a simulated light source. The samples (BSO-HNS, BSO1, BSO2), Pt wire, Ag/AgCl, and Na₂SO₄ solution (1 M) were used as working, counter, and reference electrodes, and as the electrolyte, respectively. The working electrode was prepared via the dip-coating method on indium tin oxide (ITO) and had an area 1 cm² in size. The Mott–Schottky measurements were performed at the frequency of 5 kHz. The photoluminescence (PL) spectra was carried out on a Hitachi F-4500 fluorescence spectrophotometer at room temperature and obtained with excitation wavelength at 320 nm. The ferroelectric properties of BSO-HNS were characterized by a piezoresponse force microscopy (PFM) with a conductive Pt/Ir-coated silicon tip (Type: EFM, Nanoworld. Force constant: 2.8 N/m). For the switching spectroscopy PFM (SS-PFM) measurements, a sweeping DC bias (Frequency = 0.2 Hz) in the range of ± 25 V was applied to provide BSO-HNS nanosheets with the essential electric field, and the quality factor (Q) was 288 (i.e., the gain in a weak PFM signal). During acquisition of a single curve, five cycles of sweeping triangle/square waves were applied to show reproducibility. Igor Pro 6.36 Software was used to obtain the butterfly loops and analyse the data. In each step, the DC bias was switched ON and OFF to minimize electrostatic forces, and the data was recorded while the DC bias was OFF, ensuring that the deformation of the sample was entirely due to the ferroelectric effect.

5.2.3 Photocatalytic activity evaluation

The photocatalytic activity was evaluated by the degradation of Rhodamine B (RhB) and phenol (Sigma-Aldrich), which were used as model organics pollutants in the photocatalytic degradation experiment at room temperature. A 300 W Xe lamp was used as the simulated light source for photocatalytic performance. In a typical process, 50 mL of RhB (10 mg/l) (for phenol 20 mg/l), and 0.05 g of the as-prepared sample were added together in a 100 mL beaker with a diameter of 6 cm. The suspension was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium, and then the mixture was irradiated with the light source. At certain time intervals, a 3 mL aliquot was taken and centrifuged to remove the photocatalyst. The photodegradation activity was analysed using the UV-Vis spectrophotometer by recording the variation of the peak absorption 556 nm and 269 nm for RhB and phenol respectively. To calculate the reaction kinetics $K_t$ of RhB and phenol degradation, the pseudo-first-order kinetic model was derived.

5.2.4 Theoretical calculation

All density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP) package. Generalized gradient approximation (GGA) was applied to
treat the exchange-correlation energy with the Perdew–Burke–Ernzerhof (PBE) functional and the projector augmented wave (PAW) method was employed to describe electron–ion interactions. The cut-off energy was set as 400 eV. Structures were fully relaxed until the convergence tolerance of force on each atom was smaller than 0.01 eV. The energy converge criteria was set to be $1 \times 10^{-5}$ eV for self-consistent calculations and k-point sampling was $5 \times 7 \times 7$. Isosurface is 0.01 eV/Å$^3$.

5.3 Results and discussion

The structure and element composition characterizations of the as-prepared samples were carried out by XRD and XPS. As shown in Figures 5-1,5-2 and 5-3, all the recorded peaks of BSO-HNS demonstrate the coexistence of two phases, the orthorhombic Bi$_2$SiO$_5$ phase (JCPDS: 36-0287) and the cubic Bi$_4$(SiO$_4$)$_3$ phase (JCPDS: 002-0488). The pure phases BSO1 and BSO2 are also indexed to Bi$_2$SiO$_5$ phase (JCPDS: 36-0287) and Bi$_4$(SiO$_4$)$_3$ phase (JCPDS: 002-0488), respectively. No other peaks from possible impurities were detected. To confirm the absence of any surface contamination materials, in particularly Br, the surface chemical composition of the sample was analyzed by XPS, as illustrated in Figure 5-4 a, where only the elements Bi, Si, O, and C were observed in the survey scan spectrum. For this heterostructure, the main peaks located at 158.9 and 164.3 eV correspond to Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$, respectively, whereas the peaks of Si 2p and O 1s are located at 101 and 530 eV respectively. EDS analysis of the BSO-HNS sample (Figure 5-4 b) also confirmed the presence of Bi, Si, O, and no other impurity elements have been detected. (The element carbon was from the background.)

The morphology and heterostructure features of the sample were investigated and confirmed by FESEM and TEM. Flake-like nanostructures with a thickness of 10-20 nm can be observed from the SEM image of the as-prepared BSO-HNS sample, as shown in Figure 5-5.

Figure 5-1 XRD pattern of as-prepared BSO-HNS
Figure 5-2 XRD pattern of as-prepared BSO1

Figure 5-3 XRD pattern of as-prepared BSO2
The as-prepared BSO-HNS sample with two phases shows flake structures with a thickness of 10 - 20 nm. The TEM and high-resolution TEM (HRTEM) images (Figure 5-6) show that some tiny nanocrystals with sizes of 5-8 nm are inlaid in the flake matrix. The lattice fringes show \(d\)-spacing of 0.274 nm for the flake matrix and 0.326 nm for the tiny nanocrystals, which can be assigned to the \(d\)-spacing of the (020) planes for Bi\(_2\)SiO\(_5\) and the \(d\)-spacing of (310) planes for Bi\(_4\)(SiO\(_4\))\(_3\) respectively.

Figure 5-5 FESEM images of as-prepared BSO-HNS
The SAED pattern of the as-prepared BSO-HNS [inset image (1) in Figure 5-7] further confirms the presence of Bi$_2$SiO$_5$ and Bi$_4$(SiO$_4$)$_3$. As a layered material, the side view HRTEM of the Bi$_2$SiO$_5$ sheet presents a clear layer structure with a layer spacing of 0.76 nm which is corresponding to (200) planes (see the inset image (2) in Figure 5-7). In addition, in theoretically, the angle between (200) and (020) planes is 90°, therefore, these results indicate that the top surface sheet is dominated by (100) facet.
Depending on above explanation, the crystal orientation, polarization direction and atomic configuration in the top view of (100) facets of as-prepared BSO-HNS have been determined as shown in Figure 5-8. The Bi$_4$(SiO$_4$)$_3$ phase is observed to resemble as dots that act as islands on the Bi$_2$SiO$_5$ surface, which demonstrates clear contacted at the interfaces as well as good compatibility of the lattices, indicating the formation of heterogeneous nanostructures. It is proposed that, in the one-pot hydrothermal reaction, this large 2D flat exposed surface of Bi$_2$SiO$_5$ matrix grown via the crystallization of Bi$_2$O$_2^{2+}$ and SiO$_3^{2-}$ provides a good platform for the growth of the 0D Bi$_4$(SiO$_4$)$_3$ dots by the nucleation of Bi$^{3+}$ and SiO$_4^{4-}$.

Bi$_2$SiO$_5$ has been reported to be a 2D ferroelectric compound at room temperature in previous studies [22, 23]. For the sheet-like nanostructures, the main direction of the polarization and internal electric field is parallel (in-plane) to the 2D exposed surface, whereas the weak direction of the polarization and internal electric field is perpendicular (out-of-plane) to the 2D exposed surface, which is expected to facilitate the quick diffusion of the photoinduced carries to the large exposed surface. To evaluate the ferroelectric properties of BSO-HNS, SS-PFM measurements were carried out to study the polarization in the micro-size nanosheets. Figure 5-9 a and b shows atomic force microscopy (AFM) topography and PFM amplitude images of the BSO-HNS sample, showing flake-like morphology with the flakes having a lateral dimensional size of a few microns and a thickness of 15 nm and the PFM image shows a the upward-polarized mono-domain structure and zero PFM amplitude at the boundary of the flakes. The SS-PFM measurements were carried on the spots indicated in Figure 5-9 band 5-10 a and b show the macroscopic hysteresis loops, which resemble butterfly loops, and the corresponding phase switching curves. The hysteresis amplitude – DC voltage loops are evidence of ferroelectric behavior with 180°
switching of the phase. Minimal deformation was exhibited at the phase-switching DC bias, which means that responses from the nascent domains generated by the tip bias and the surrounding material are compensating each other [27].

Figure 5-9 SS-PFM results on the BSO-HNS sample: (a) AFM topography with a white line cutting cross-section the flake profile with a step height of 15 nm; image scale: 5 × 5 μm², (b) PFM amplitude image (white letters a and b represent the flake and substrate area respectively.

The deformation response and phase switching were both stable within the five cycles of measurement, indicating the reversible nature of the ferroelectric polarization. Non-symmetric coercive voltages were observed in range from 10 to -20 V in amplitude (Figure 5-10 a and b), corresponding to the non-symmetric coercive voltages in the phase, since the electrostatic contribution between the tip and the surface of the sample can lead to asymmetry in the hysteresis loop curves [28]. The piezoelectric coefficient \( d_{zz} \) for the out-of-plane direction was calculated from the relationship between the amplitude \( L \) \( \text{(i.e. the surface displacement or deformation)} \) and the AC applied voltage, \( V_{ac} \). \( d_{zz} \) can be obtained from following equation [29]:

\[
d_{zz} = \frac{L}{Q \cdot V_{ac}}
\]

where \( Q \) is the quality factor that describes the gain in a weak PFM signal in the system (Asylum Research), \( V_{ac} = 200 \text{ mV} \) and \( L = 500 \text{ pm} \) on average at 10 DC bias which calculated from hysteresis loop. The obtained piezoelectric coefficient \( d_{ij} \) is 8.7 pm/V, which is slightly lower than the \( d_{zz} \) of BSO bulk (11 pm/V out-plane) in Ref. [30]. The low \( d_{zz} \) value is attributed to less thickness, which, in turn, leads to low effective domains. For comparison, the same measurement was also conducted on the substrate. The amplitude loops only showed noise, and no phase switching was observed, which confirmed the butterfly loop generated from the ferroelectric sample (Figure 5-11 a and b). Based on the above discussion, it is confirmed that the BSO-HNS heterostructures remain ferroelectric in the nanoscale.
Figure 5-10 (a) PFM amplitude and (b) phase hysteresis loops for 5 cycles of the BSO-HNS sample.

Figure 5-11 PFM amplitude and (B) phase curves of as-prepared BSO-HNS for 5 cycles of sweeping triangle/square waves on the substrate, the measurement was also conducted on the substrate.

The diffuse reflectance spectra of the BSO-HNS, BSO1, and BSO2 samples were collected to evaluate the optical properties of the as-prepared samples. According to their spectra (Figure 5-12), all three samples have light absorption capability in the UV light region. The band gaps of the samples were estimated from the onsets of the absorption edges by using the Tauc formula [31].
As shown in the upper right inset image of Figure 5-11, the calculated band gaps are 3.5 eV, 3.3 eV, and 3.0 eV for BSO1, BSO-HNS, and BSO2, respectively. Obviously, the as-prepared BSO-HNS sample with 0D Bi$_4$(SiO$_4$)$_3$ dots on the Bi$_2$SiO$_5$ surface possesses stronger light absorption capability than pure Bi$_2$SiO$_5$.

The photocatalytic activity of the BSO-HNS sample, as well as the BSO1 and BSO2 samples, was evaluated by degrading organic compounds under simulated solar light. RhB dye and phenol were used here as a colorful dye pollutant and a typical colorless contaminant, respectively. Before photocatalytic reaction, adsorption performance of three samples BSO1, BSO-HNS and BSO2 have carried out in the dark in the interval 30 min for each RhB and phenol. The three samples were compared as shown in Figure 5-13. From Figure 5-13 the adsorption performance of the three samples reached their saturation within 30 min. It is clearly shown that BSO1 has maximum adsorption for RhB and then BSO2 and BSO-HNS respectively, whereas the lower adsorption performance has shown in phenol in three samples. For the photocatalytic degradation test, as shown in Figure 5-14 and 5-15. The BSO-HNS sample exhibited the best efficiency toward the photodegradation of RhB. The concentration of RhB relative to the absorption intensity at 556 nm decreased rapidly with increasing irradiation time and nearly reached zero within 50 min. In contrast, only 30% and 15% of the RhB were decomposed under irradiation for 50 mins over the BSO1 and BSO2 samples, respectively.
Figure 5-13 Adsorption performance of three samples BSO1, BSO-HNS and BSO2 has carried out in dark in interval 30 min for each RhB and phenol.

Figure 5-14 UV-Vis absorbance spectra of the photodegradation of RhB dye by BSO-HNS under UV-Vis light, recorded after different degradation times.

To further explain the reaction kinetics of photocatalytic degradation, the pseudo-first-order linear relationship is shown in the inset image of Figure 5-15. The constant rate $k$ is 0.064 min$^{-1}$ for BSO-HNS, which is much higher than those of BSO1 (0.0089 min$^{-1}$) and BSO2 (0.0032 min$^{-1}$). This suggests that the photocatalytic activity of the 0D-2D heterostructures is about seven times higher than for either of the pure phase samples. The photodegradation of phenol reached 35% in the presence of the BSO-HNS sample after 150 mins under simulated solar light irradiation, as shown in Figure 5-16, which demonstrates this sample’s good photocatalytic activity towards the degradation of a colorless contaminant.
The photocatalytic durability of the BSO-HNS sample was evaluated by recycling the sample after photodegradation. After each cycle, the catalyst was collected by centrifugation, as shown in Figure 5-17 a. The decline in the photocatalytic activity was only 3.7% after 5 cycles over more than 4 hours, indicating the high stability of the photocatalytic activity of BSO-HNS. To further evaluate the chemical stability of the catalyst, XRD and XPS analysis of the BSO-HNS sample after five cycles of photocatalytic reaction were carried out. As shown in Figure 5-17 b, all the main peaks for Bi$_2$SiO$_5$ and Bi$_4$(SiO$_4$)$_3$ remain. The XPS results (Figure 5-18) show no obvious shift for all the characteristic peaks, indicating no valence change for the elements in this composite, which indicates the good stability of this heterogeneous system.
Figure 5-16 photodegradation rate of phenol by BSO-HNS under UV-Vis light, with the inset showing the UV-Vis absorbance spectra of the degradation of phenol.

Figure 5-17 5 recycling runs to test the degradation of RhB by BSO-HNS under UV-Vis light; (b) XRD patterns before and after 5 cycling runs to test the photodegradation of RhB by BSO-HNS under UV-Vis light.

In comparison with the pure Bi$_2$SiO$_5$ and Bi$_4$(SiO$_4$)$_3$ samples, the BSO-HNS sample shows a significant enhancement in its photocatalytic activity, which may attribute to the more efficient separation of the photoexcited electron-hole pairs in the as-prepared 0D-2D heterogeneous structure.
To verify this, as shown in Figure 5-19, the photocurrent response of the different samples was investigated under intermittent light illumination (same wavelength range as that used in the photocatalytic reactions). It can be clearly seen that the photocurrent for the BSO-HNS electrode increased/decreased rapidly as the light was turned on/off. The transient photocurrent responses of BSO-HNS electrode were quite stable and higher by three times than those of BSO1 and BSO2 electrodes. It is well known that enhancement in photocurrent response originates from improved photoinduced charge separation. In view of the negative photocurrent responses produced under the bias applied to the working electrodes in the electrochemical system here, the photocurrent was produced mainly by the diffusion of the photogenerated holes to the ITO. Meanwhile, the electron acceptor in the electrolyte took up the photoinduced electrons. Therefore, the enhanced transient photocurrent response of BSO-HNS indicates a more efficient separation of the photoinduced electron-hole pairs or a longer lifetime of the photogenerated charge carriers as compared to the BSO1 and BSO2.

To further confirmation of charge separation, the PL spectra were carried out with excitation light 320 nm. The PL results of BSO-HNS and BSO2 samples as shown in Figure 5-20, the higher intensity emission spectra of BSO2 compare with BSO-HNS, indicating that BSO-HNS has higher charge separation compare with BSO2.
The synergistic effects of high polarization in the 2D ferroelectric Bi$_2$SiO$_5$ nanosheets and the band bending at the 0D-2D interfaces of the heterostructures is believed to be the most important factor behind the enhanced photocurrent response and photocatalytic performance of the BSO-HNS sample. To reveal the mechanism of the enhanced photocurrent response and improved photocatalytic activity of BSO-HNS, the band-structure properties and ferroelectric properties of the samples were investigated.

The band positions including the conduction band ($E_{CB}$) and the valence band ($E_{VB}$) for BSO-HNS, BSO1, and BSO2 were examined by Mott-Schottky measurements [32], as shown in Figure 5-21. The flat-band potentials ($E_b$) of BSO-HNS, BSO1, BSO2 are estimated to be $-0.96$, $-0.92$ and $-0.94$ V (vs. Ag/AgCl), respectively, or $-0.76$, $-0.72$, and $-0.74$ V (vs. normal hydrogen electrode (NHE)) by Mott–Schottky analysis. These negative values and the positive slope indicate $n$-type semiconducting properties for these three samples, $E_b$ is considered to be located
just under the conduction band. Thus, based on the calculated band gaps mentioned above, a band
diagram of the BSO-HNS heterostructure with the valence band and conduction band edge
positions was constructed. As shown in Figure 5-22, the band bending between Bi$_2$SiO$_5$ and
Bi$_4$(SiO$_3$)$_3$, in this system transfers the photoinduced electrons in the 0D Bi$_4$(SiO$_3$)$_3$ to the surface
of the 2D Bi$_2$SiO$_5$, and the holes are transferred from 2D Bi$_2$SiO$_5$ to Bi$_4$(SiO$_3$)$_3$.

![Mott–Schottky plots of BSO-HNS, BSO1, and BSO2.](image)

This heterostructure results in high charge-separation efficiency in the localized areas of the 0D-
2D interface, which would not only significantly improve the separation/diffusion rate of the
photogenerated charge carriers, but also strongly affects the polarization of the 2D Bi$_2$SiO$_5$ matrix.
For further photocatalytic mechanism, it has been proven in literature that internal electric field
(IEF) (include spontaneous polarization) can promote charge separation [1, 3, 5, 33], particularly
Bi-based photocatalyst [34], and the IEF direction in nanosheet has shown different photocatalytic
activity. According to literature, the IEF perpendicular to the [Bi$_2$O$_2$]$^{2+}$ slabs (i.e. perpendicular on
c-axis) has more photocatalytic activity than IEF generated parallel along [Bi$_2$O$_2$]$^{2+}$ slabs because
shorter diffusion distance of charges to reach the surface [35-37].
Figure 5-22 Schematic diagram of the redox potentials of BSO1, BSO2 and Possible photocatalytic mechanism of the BSO-HNS sample according to the Mott–Schottky and DRS spectroscopy results.

In our sample, it has been reported that IEF is perpendicular to the [Bi₂O₂]²⁺ slabs as well as main IEF generated parallel along [Bi₂O₂]²⁺. Therefore, we carried out theoretical calculation as shown in Figure 5-23 to confirm polarization on (100) facet which it is believed that polarization can promote charge separation. This result suggests that the spontaneous electric polarization in Bi₂SiO₅ is attributable to misaligned positive and negative charge centers, it was confirmed [22] there are out-plan and in-plan polarization in Bi₂SiO₅ and each polarization direction has a role in charge separation. Beside IEF, the heterostructure based IEF have shown higher charge separation [38, 39]. The photo-generated charge electron-hole pairs which separated by out-plan polarization can reach surface and interface surface where there is the band bending at the 0D-2D interface of the heterostructure [38].

Figure 5-23 Charge density map of (100) facet of BSO-HNS

Some holes would be injected to lower positive potential of VB of Bi₄Si₃O₁₂ in the interface
Consequently, the charge electron-hole pairs have been separated. On the other hand, the excited electron in Bi$_4$Si$_3$O$_{12}$ could be injected to Bi$_2$SiO$_5$ surface and move away from Bi$_4$Si$_3$O$_{12}$ due to effective in-plan polarization in (100) facet [39]. However, more explorations are needed in future to further clarify photocatalytic mechanism because of the complexity of interfacing semiconductor with ferroelectric materials.

5.4 Conclusion

In summary, 0D–2D bismuth silicate based heterostructures were successfully synthesized by the in situ growth of 0D Bi$_4$(SiO$_4$)$_3$ dots on 2D Bi$_2$SiO$_5$ nanosheets via a one-pot hydrothermal process. The heterogeneous photocatalyst exhibits much enhanced photocatalytic activity towards the degradation of RhB under simulated solar light irradiation, which is seven times higher than for either of the pure phase samples. The enhanced activity is attributed to the effective separation of electron–hole pairs due to the synergistic effects of polarization in the ferroelectric Bi$_2$SiO$_5$ nanosheets and the band bending at the 0D–2D interface of the heterostructures. Such a composite photocatalyst is promising for water purification applications and environmental remediation.

5.5 References


Selective deposition of BiOI on the positive polar surface of Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} by the polarization-adsorption effect and evaluation of the photocatalytic performance

6.1 Introduction

The high recombination rates of photogenerated electron-hole pairs inside the bulk of a photocatalyst, the back-reactions of intermediate species, and inactivity towards visible light are regarded as the key issues blocking light-conversion efficiency. The driving force of charge separation (DFCS) via an internal electric field (IEF) plays a key role in reducing recombination rates [1-5]. The IEF that is in the p-n junction, unfortunately, only exists in the space charge layer (due to band bending generated after contact between the n and p sides due to different Fermi energy levels and different semiconductor types). Overall, according to a review on heterojunctions, the enhancement of photocatalytic activity is not high [6]. The DFCS that is provided by the ferroelectric photovoltaic effect (FPV) has demonstrated its ability to create high photovoltage due to enhanced charge separation [7, 8]. This kind of nano-polycrystalline material with disordered domains shows low photocatalyst activity, however, unless the IEF is controlled (i.e. the polarization is orientated in the ferroelectric). It is confirmed that FPV produces spatially separated oxidation/reduction (redox) sites on surfaces, and thus, it can reduce the back-reactions on the surfaces and recombination [9]. To switch the polarization of a ferroelectric, an external electric field is applied on the photoelectrode, therefore poling the polarization direction up and down, according to the sign of the external electric field [10-13]. Nevertheless, control of polarization has only been carried out in films. A ferroelectric-semiconductor (F-S) with a band gap in the visible range, such as Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} (BTO) and BiFeO\textsubscript{3} have been considered attractive because they combine optoelectronic and ferroelectric properties [14-17]. Single crystal BTO nanoplates prepared from molten salts have shown much higher photocatalytic activity with the assistance of FPV [18-20]. The single crystal plate provides faceted surfaces, pathways for electronic charge carriers and selective photodeposition, monodomain or longer disordered chains in the crystal structure, and spatially separated redox positions on surfaces. Because of the BTO-based layered structure, anisotropic behaviour is present, along with the presence of higher polarity for the \textit{ab}-plane than along the \textit{c}-axis in BTO [16, 21]. The anisotropy in BTO is not only in polarization, but also in the light absorption coefficient. It has been confirmed that the band gap in BTO with (001) facet is a lower band gap than in the polycrystalline material [22]. The polarization potential can be screened by charges which either come from the bulk of the ferroelectric or from the environment (usually, a liquid, since the liquids contain many Ions, cations, and polar molecules) and then generate a Stern layer causing charge separation. The previous reports have studied the F-S/S interface to form junctions [11, 13]. Nevertheless, few have studied F-S/S nanostructures in powder form with the growth controlled over the specific
polarization potential. In this work, we explore a new concept to form a heterojunction built-in DFCS that has a positive polarization of BTO interfaced with an n-type semiconductor such as BiOI in order to charge transfer. BiOI works as an electrons transporter for the electrons coming from BTO due to its having a lower conduction band than BTO and a layered crystal structure (including Bi$_2$O$_2^{4+}$ slabs for each BiOI and BTO) and also a narrow band gap and easy growth. The polarization-adsorption interaction is important for selective deposition on the surface. It has been proven that the polar surface of a ferroelectric adsorbs ions and polar molecules from a solution [23, 24], which then can undergo easy epitaxial growth as a photocatalyst [25]. Spatially selective deposition under illumination can be also observed for the deposition of metals (including Ag, Au, Pt, etc.) on the positively polarized boundaries of a ferroelectric surface [9], and photocatalytic activity is significantly enhanced compared to deposition by a conventional loading method where there is disorder in the interfacing materials. Moreover, photodeposition can explore the pathways of electron-hole and redox position surfaces. We propose in this work that this represents a new strategy to enhance photocatalytic activity and open up opportunities for further exploration of ferroelectric-semiconductor/semiconductor interfaces.

6.2 Experimental

6.2.1 Synthesis of sample

The BTO plates were synthesised by the molten salt method. The BTO plates were prepared in as in a previous reports by mixing bismuth oxide and titanium oxide with salts, but here, we used little modification, and we prepared amorphous BTO powder by wet reaction of the raw materials and then mixing them with salts. It was believed that this modification is easier than in previous reports because it doesn’t need much mixing and requires a shorter time for reaction. In a typical experimental process: Bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O, Sigma-Aldrich) and titanium butoxide (C$_{16}$H$_{36}$O$_4$Ti, Sigma-Aldrich) were used as raw materials. A typical synthesis for BTO plates is described as follows: 4 mmol of Bi(NO$_3$)$_3$·5H$_2$O was dissolved into a solution of 20 ml ethylene glycol and 40 ml absolute ethanol, and then 3 mmol of C$_{16}$H$_{36}$O$_4$Ti was dissolved in the above solution drop by drop. The pH was adjusted by adding KOH up to pH = 10. The clear solution changed to a white precursor under stirring, and it was kept under stirring for 4 h before being filtered by centrifuge. The white powder was washed many times with water and ethanol. Amorphous BTO was obtained after drying for a day. The weight ratio was 10 g : 1 g of the salts (NaCl: KCl = 1:1) to the powder. The mixture was been mixed in a mortar for 5 min and then sintered for 1 h at 750 °C and cooled naturally to room temperature. The product was washed many times by water and ethanol to remove salts and then dried.

6.2.2 Selective photodeposition of metal/metal oxide on BTO plate:

Photoreduction was carried out at room temperature with no change in pH. A typical 1 ml of AgNO$_3$ (0.1 M AgNO$_3$), which was used in the reduction process to deposit Ag, was added to a BTO solution (0.1 g BTO was dispersed in 50 ml distilled water + 2 ml methanol). The suspension was stirred for 0.5 h and then irradiated under a 300 W Xe lamp without an optical filter for 6 h. After that the suspension was filtered and washed, and finally dried at 60 C. Photooxidation was
also carried out by the same procedure above, in which 1 ml of MnSO$_4$ (0.1 M MnSO$_4$) was used for the oxidation process to deposit MnO$_x$. It was added into a solution containing KIO$_3$, and the irradiation time was 0.5 h.

**6.6.3 Selective deposition of BiOI on BTO plate:**
Because of the polarity behaviour of the ferroelectric, 0.1 g of BTO powder was dispersed in 20 ml ethylene glycol and then 150 ml of distilled water was added under sonication for 2 min, and then the dispersion was stirred for 10 min to prepare the BTO suspension. Two solutions, one of sodium iodide and a bismuth nitrate solution, were prepared separately. 1 mmol of NaI was dissolved in 50 ml of distilled water, and Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 15 ml ethylene glycol, followed by the addition of 35 ml water. Firstly, 0.25 ml of NaI solution was added to the BTO suspension, which was then kept under stirring for 15 min before 0.25 ml of Bi(NO$_3$)$_3$·5H$_2$O solution was added to the suspension and it was again kept under stirring for 15 min. The above procedure was continued with the addition of NaI and Bi(NO$_3$)$_3$·5H$_2$O until the amount became 0.75 ml for each. The colour of the suspension changed from white to light yellow, and this sample was labelled as BTO-BI-1. For a greater BiOI concentration, more NaI and Bi(NO$_3$)$_3$·5H$_2$O solutions were added into the above suspension to achieve 1.25 ml and 1.75 ml of BiOI for the next to samples, respectively, and the results were labelled as BTO-BI-2 and BTO-BI-3, respectively. The colour of the samples (BTO-BI-1 and BTO-BI-2) was changed from light yellow to yellow and yellow-orange, respectively. For comparison, the BTO-BI-3 was also prepared by a conventional loading method. Typically, 1.75 ml NaI solution was added to the above suspension and then 1.75 ml Bi(NO$_3$)$_3$·5H$_2$O was added, which was previously solved in water, and it was kept under stirring for 15 min and labelled BTO-BI-X. All samples were finally washed and then dried. For pure BiOI, the same procedure above was followed without BTO powder.

**6.6.4 Characterization**
The purities and crystal structures of the samples were investigated by X-ray diffraction (XRD, GBC, MMA) using Cu Kα radiation. The sample morphology was investigated and the elemental analysis performed by field emission scanning electron microscopy (FESEM, JEOL-7500). The composition of the samples was examined by using an energy dispersive spectroscopy (EDS) instrument coupled to the FESEM. The valences of elements were studied by X-ray photoelectron spectroscopy (XPS, PHI660), which was performed using a monochromatic Cu Kα X-ray source. Morphologies and structures were further examined by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) (JEOL, JEM-2010). An ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu-3600) was used to collect diffuse reflectance spectra (DRS) with an integrating sphere attachment to the instrument, with BaSO$_4$ providing a background between 200 nm and 800 nm.

**6.6.5 Thin film preparation**
The thin films of BTO, BTO-BI-1, BTO-BI-2 and BTO-BI-3 were prepared via a metering rod on fluorine-doped tin oxide (FTO) substrates that had an area of 2.5 cm$^2$. The substrates were previously cleaned with ethanol under sonication for 10 min. 0.005 g of powder was mixed with a
binder material such as 4-5 µl of N-methyl-2-pyrrolidone (NMP) and mixed in a mortar for 15 min until the mixture became a paste. The metering rod method was used to prepare the thin films with an area of 1 cm², and they were then annealed at 150 °C for 3 h, which provided them with mechanical stability. BTO thin films with positive poling, no poling, and negative poling were prepared according to ref. [26] and then the polarization was switched in the opposite direction by an applied external voltage, whereas the BiOI/BTO photoanodes were prepared by the growth of BiOI on BTO thin film by the successive ionic layer adsorption and reaction (SILAR) method.

**Electrochemical and photoelectrochemical measurements**

The transient photocurrent, the photovoltage decay and the flat band potential were collected with a VSP-300 potentiostat, and a 300 W Xe lamp was used with a UV-optical filter. The samples (BTO, BTO-BI-1, BTO-BI-2, and BTO-BI-3), Pt wire, Ag/AgCl (KCl 3 M), and Na₂SO₄ solution (0.1 M) were used as the working electrode, counter, and reference electrodes, and as the electrolyte, respectively. The on-off light response was collected every 30 seconds by chopped light for transient photocurrent measurements by chronoamperometry (CA) (bias voltage = 0 V), whereas the photovoltage decay time was measured after light-off, using the open circuit voltage technique (OCV). The flat band potential was measured according to The Mott–Schottky (MS) method, which was performed at a frequency of 1 kHz in the dark at room temperature, and the impedance was measured in the frequency range of 100 KHz to 0.05 Hz with applied voltage of 5 mV in the dark and under light, using electrochemical impedance spectroscopy (EIS).

**6.6.6 Photocatalytic activity evaluation**

The photocatalytic activity was evaluated by the degradation of Rhodamine B (RhB) and phenol (Sigma-Aldrich), which were used as model organic pollutants in the photocatalytic degradation experiment at room temperature. A 300 W Xe lamp with cut-off filter (λ > 420 nm) was used as the light source for studying the photocatalytic performance. In a typical process, 25 mL of RhB (10 mg l⁻¹) (or phenol 20 mg l⁻¹), and 0.025 g of as-prepared sample were added into a 100 mL beaker with a diameter of 6 cm. The suspension was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium, and then the mixture was irradiated by the light source. At certain time intervals, a 3 mL aliquot was taken and centrifuged to remove the photocatalyst. The photodegradation activity was analysed using the UV-Vis spectrophotometer by recording the variation of the peak absorption at 556 nm for RhB and 270 nm for phenol. For comparison with other dyes, Methylene blue (MB) and Methylene orange (MO) were used for comparison with RhB.
6.3 Results and Discussion

According to our procedure, the BTO powder was prepared using molten salts, and the colours of the BTO-BI-1, BTO-BI-2, and BTO-BI-3 heterojunction samples were changed from milky to milky-yellow, yellow, and yellow-orange, respectively on increasing the BiOI content.

The sample characterizations were first conducted by X-ray diffraction (XRD) to analyse the crystallinity and purity. The XRD patterns of the as-prepared samples, as shown in Figure 6-1(a), indicate high crystallinity. All the diffraction peaks can be indexed to orthorhombic Bi₄Ti₃O₁₂ (space group B2ab) and were without any observable impurities, consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) Card no. 01-089-7500. In the XRD pattern of BTO-BI-3, the BiOI diffraction peaks are clearly observed which are 29.7° and 31.7°, assigned to the (012) and (110) planes of tetragonal BiOI (JCPDS: 90-901-1785), whereas peaks of BiOI were not observed in BTO-BI-1 and BTO-BI-2 because of the low content. Because the diffraction peaks related to BiOI have not been demonstrated in XRD, except for BTO-BI-3, XPS was conducted to confirm the chemical states and chemical compositions of the samples. The survey
spectrum for the BTO sample reveals that it only contains Bi, Ti, and O elements without any impurity (Figure 6-1(b)) whereas in the heterojunctions, the samples include I element. The high-resolution results demonstrate that the two peaks with binding energy at 164 and 158.6 eV correspond to Bi 4f5/2 and Bi 4f7/2 of Bi^3+ in the crystal (Figure 6-1(c)), respectively and there is a slight shift in the binding energies in the heterojunctions. The binding energy was shifted to higher binding energy toward pure BiOI with increasing BiOI content. The peak at 528.9 eV is assigned to O 1s (Figure 6-1 (d)), and this peak could be deconvoluted into three peaks with binding energies of 528.9, 529.2, and 531.7 , which correspond to Bi-O, Ti-O, and adsorbed hydroxyl groups. The binding energies of the heterojunctions were shifted up. Moreover, a small peak at 155.5 eV is assigned to oxygen vacancy. Which is seen in each both pure BiOI and pure BTO. The peaks at 630.3 eV and 618.8 eV are assigned to I 3d3/2 and I 3d5/2, respectively, and the chemical state is I^-1. There was no shift in the binding energy with decreasing BiOI content. The binding energy peak at 457.1 eV is assigned to Ti 2p3/2, whereas the Ti 2p1/2 peak overlaps with Bi 4d3/2 at 462.8 eV with the chemical state Ti^4+. The Ti 2p peaks were not clearly shifted with increasing BiOI content. On comparing the XPS spectrum of pure BTO with that of a BTO/BiOI heterojunction, the elements Bi and O were shifted up in binding energies with no contribution from Ti and I, which could indicate that that Bi-O bonds of BTO interacted with the Bi-O bonds of BiOI. They possess different electronegativity, and electrons transfer between them results in band bending. The morphology of the samples was observed by FESEM and TEM images. The FESEM image reveals that the as-prepared BTO sample consists of micron-sized plate-like particles with a thickness of 50-60 nm (Figure 6-2(a)). The heterojunction samples BTO-BI-1, BTO-BI-2, and BTO-BI-3 were also observed by FESEM. as shown in Figure 6-2(b), (c), and (d). It can be seen that the BiOI has only grown at the edge of the BTO plates, and the growth of BiOI increased with an increasing amount of NaI/Bi(NO3)3·5H2O solution in the reaction. In the BTO-BI-3 almost all the edges of BTO appear to be covered, as shown in Figure 6-2(d), which was investigated by EDS to find the elemental contents and distributions. Figure 6-2(f), (j), (d), (h), and (i) corresponds to Bi, I, Ti, and O respectively. The TEM image shown in Figure 6-2(g) is more confirmation of the morphology shown by the FESEM image. The single crystal nature of the Bi4Ti3O12 plates is confirmed in the SAED pattern shown in Figure 6-2(k), and the top view surfaces of the BTO plates are exposed (001) facets, which were determined from the theoretical interfacial angle of 90° between the (020) and (200) planes. The (004), (003), and (011) planes indicated by the yellow lines in the Figure confirm the presence of BiOI in area enclosed by the yellow square in Figure 6-2(g). For further confirmation, high resolution TEM (HRTEM) was conducted to observe the same yellow area, and the BiOI shows (001) facets. The results for both BTO and BiOI indicate exposed (001) facets. It should be noted that there is large spontaneous polarization along the a-axis due to distortion of the entire TiO6 octahedral layer with respect to the Bi ions, and thus the edges of BTO show polarity [3]. According to previous results on BTO and our results from HRTEM and XPS, the mechanism for the growth BiOI on the edges of BTO could be explained. A physisorption interaction exists between the terminal edge of BTO and the I^-1 present with Bi^3+ in solution. Because of the permanent polarization of BTO, electrostatic interaction (van der Waals forces)
occurs between positively polarised BTO and the negative ions in solution, resulting in screening of the positive polarization. Next, when the chemical force exists between the adsorbed substance and the terminal edge of BTO in the presence of Bi$^{+3}$, chemical reactions occur, forming chemical bonds attaching BiOI to the BTO edge; the process is called chemisorption.

The photocatalytic activity of the samples was evaluated by decolouration of organic dye under visible light. RhB dye was used as a colourful dye. Before the photocatalytic reaction, the adsorption performance of all samples was investigated in the dark after an interval of 30 min. The samples were compared, as shown in Figure 6-3(a), and it was found that the adsorption performance of the samples reached saturation within 30 min and exhibited high adsorption efficiency, possibly due to the polar surface of BTO. In addition, there are no significantly different results between the samples in the adsorption process. The BiOI-BI-2 and BiOI-BI-3 samples exhibited the best efficiency toward the photodegradation of RhB, and because the BiOI-BI-2 showed very close results to BiOI-BI-3, it has been neglected throughout the Figures. A typical visible absorbance spectrum of RhB degradation by BTO-BI-3 is shown in Figure 6-3(b), where the concentration of RhB is relative to the intensity of peak absorption at 556 nm, which decreased rapidly with increasing irradiation time and nearly reached zero within 12 min (Figure 6-3(b)).
Figure 6-3 Photodegradation rates for the RhB dye by all samples under visible light. (b) Typical visible absorbance spectra of the photodegradation of the RhB dye by BTO-BI-3 under visible light, recorded after different degradation times. (c) Photodegradation rates of BTO, BTO-BI-1, and BTO-BI-3 for phenol within 60 min. (d) Adsorption performance of BTO, BTO-BI-1, BTO-BI-2, and BTO-BI-3 carried out in the dark after an interval of 30 min for RhB and MO. (e) comparison of photodecolouration rate percentage of the RhB, MB, and MO dyes achieved by BTO and BTO-BI-3 for different irradiation times under visible light. (f) Comparison of the photodegradation by BTO-BI-3 and BTO-BI-X for RhB after 10 min.
The colourless and toxic pollutant phenol was used to evaluate the photodegradation performance of the samples over 60 min, and the results demonstrated that 47% of phenol was photodegraded during the 60 min by BTO-BI-3, as shown in Figure 6-3(c), which indicates that BTO-BI-3 has excellent performance towards photodegradation of phenol. In contrast, only 12% and 20% phenol degradation were achieved by BTO and BTO-BI-1, respectively, under visible irradiation for 60 min. A comparison of the photodecolouration rate for other dyes with different cations and anions, MB and MO dyes, respectively, was carried out using BTO and BTO-BI-3 with different irradiation times under visible light. The adsorption results showed (Figure 6-3(d)) excellent adsorption of RhB with adsorption capacity ($Q_e$) of about 5 mg/g compared with 0.5 mg/g for MO. The photodegradation rates of cationic dyes (RhB, Crystal Violet (CV), and MB) for the BTO and BTO-BI-3 samples were significantly higher than those for the anionic dyes (MO, Orange G (OG), and Alizarin Yellow (AY)) (Figure 6-3(e)). The surface polarity of the sample could be behind the selective adsorption. The cationic dyes are highly adsorbed due to negative potential of polarization in BTO because this group of dyes carry a positive charge in their molecules when they are dissolved in water. Therefore, zeta-potential measurements ($\zeta$) were conducted in deionized water (pH = 7) at room temperature. The results revealed that BTO had a negative value ($\zeta = -12$ mV), indicating that BTO has negative surface. It is believed that photodegradability of the negative polarization surface has higher activity than the positive polarization due to significantly different photodegradation activity.

![Figure 6-4](image)

Figure 6-4 (a-f) SEM image of BTO-BI-X sample, full spectrum EDS mapping of BTO-Bi-X and EDS mapping of Ti, Bi, I, and O, respectively.

To further analyse the reason for the superior enhancement shown by BTO-BI-3, a comparison has carried out between BTO-BI-3 that was grown by our method and BTO/BiOI prepared by the conventional loading method with the same content of BiOI. The result, as shown in Figure 6-3(f), is that BTO-BI-3 has much higher photodegradation performance than BTO-BI-X (conventional...
loading method) due to the randomly growth BiOI on BTO, as shown in Figure 6-4, which shows the EDS mapping of the BTO-Bi-X sample. The wrong type of deposition, for example, not whole area deposition of the CB of BiOI on the CB of BTO or vice versa, cannot lead to enhancement in charge separation. Beside this, the growth of BiOI on the BTO surface blocks the visible spectrum for BTO.

The selective photodeposition of Ag on BTO has been carried out under UV-vis light to study charge separation and polarization behaviour. The results as shown in Figure 6-5(a) confirm that the positive potential edge due to polarization in BTO attracts electrons which are photogenerated under light, and electrons transferred at the edge react with Ag⁺, resulting in the deposition of Ag nanoparticles on the edge of BTO. Figure 6-5(b) and (c) are further confirmation of the identity of Ag metal. In addition, the photooxidation process deposits MnOₓ on the top and bottom surfaces of BTO. Thus, it can be confirmed that this ferroelectric material can separate photoinduced electrons and holes and also possesses spatially separated oxidation/reduction sites.

Figure 6-5 (a) Scanning electron microscope (SEM) images of BTO plate with photodeposited Ag on positive potential of polarization. (b) TEM image of deposited Ag on BTO. (c) SAED pattern of the inside of the yellow rectangle in the TEM image in (b), and (d) SEM image of photodeposited MnOₓ on BTO.
By macroscopically quantifying the amount of Ag:MnO\(_x\), it is possible to observe the reactivity of photoreduction and the photooxidation rate. The amount of photodeposition of MnO\(_x\) during over 0.5 h of reaction is higher than for Ag over 6 h of reaction, thus indicating that photooxidation is much more reactive than photoreduction. It has confirmed by Kelvin probe force microscopy (KPFM) in [18] with the same synthesis method and morphology that a higher positive potential was found at the edge of BTO with difference voltage potential in dark and light is 23 mV.

The on-off photocurrent was used to investigate charge separation in the samples. The photocurrent density was multiplied by at least six times because of the high charge separation of BTO-BI-3 compared with BTO, as shown in Figure 6-6(a), and the photocurrent result is in agreement with the photocatalytic activity. The electron recombination was further investigated by photovoltage decay in the on-off light conditions. The decay time is related to the charge lifetime and is considered as indicating the recombination rate level. The results are consistent with the photocurrent results (Figure 6-6(b)), with BTO-BI-3 showing the slowest decay time, also consistent with the photocurrent results.

To reveal the reason behind this enhancement, the band-structure properties of the samples, including BiOI, need to be studied. The optical properties of the samples were investigated by the diffuse reflectance. According to the absorption spectra (Figure 6-6(c)), all the samples show visible light absorption, and then there is a shift to red light spectra from BTO to BTO-BI-3 on increasing the BiOI content. The band gaps of the samples were estimated from the onsets of the absorption edges by using the Tauc formula. As shown in the upper right inset image of Figure 6(c), the calculated band gaps are 3.05 eV, 2.54 eV, 2.1 eV and 2 eV for the BTO, BTO-BI-1, BTO-BI-2, and BTO-BI-3 samples, respectively. The valence and conduction band positions were determined by Mott-Schottky measurements. The flat-band potential (\(E_{fb}\)) value is important for determining the Fermi level, because the \(E_{fb}\) has been considered nearly equal to the Fermi level.

For \(n\)-type semiconductors, the Fermi level is considered lower than the conduction band by 0.3-0.1 V. The \(E_{fb}\) values of the BTO and BiOI films were estimated, as shown in Figure 6-6(d), to be -0.66 and -0.59 V vs. Ag/AgCl (0.1 M KCl) corresponding to -0.372, -0.302 V vs. normal hydrogen electrode (NHE), respectively. These positive slopes indicate \(n\)-type semiconducting properties of these samples. Thus, the conduction bands are at -0.472 and -0.402 V and from the band gap estimates (where the BiOI band gap was considered to be 1.8 eV according to previous reports), the valence bands are 2.57 and 1.4 V, respectively. A typical BTO/BiOI heterojunction is useless because the conduction band of BiOI is lower than that of BTO, and the valence band of BiOI is lower than that of BTO, so that electrons and holes will collect in the BiOI, and thus, higher charges recombination is expected. Herein, a single type of charge transfer from BTO to BiOI is useful for charge separation, as shown in Figure 6-6 (d), the IEF that is provided by FPV is the driving force that pushes the electrons to the edges of BTO plates. Because the BTO is \(n\)-type, however, it is believed that some majority charge carriers (electrons) are driven to the positively polarised regions of BTO, and because the edge of BTO, which is [110], has a very narrow surface with a small surface area (as shown in scanning electron microscope (SEM) and HRTEM.
images), thus the positive pole of the polarization is roughly eliminated, resulting in low effective positive polarization. It is thus expected to exhibit low effective efficiency compared with the large area of {001} of BiOI. Thus, BiOI provides a larger surface area with extra electron pathways.

Figure 6-6 (a) On-Off photocurrent and (b) photovoltage decay for samples under visible light. (c) UV-vis diffuse reflectance spectra of BTO, BTO-BI-1, BTO-BI-2, and BTO-BI-3 plates, with the inset at the top right of (c) the derivation of the band gap values of the four samples, which are derived from the diffuse reflectance spectra. (d) MS plots of BTO and BiOI.
Furthermore, to further investigate the interfacing positive/negative poles of BTO with BiOI, a BiOI/BTO photoanode with different switching polarization was prepared to measure the photocurrent, open circuit voltage ($V_{oc}$), EIS spectra, and MS. The results are shown in Figure 6-6, where there is higher photocurrent by positive poling than with the negative poling and no poling photoanodes. Also, the positive poling led to a higher $V_{oc}$ than for no poling or negative poling.

EIS is important to investigate the charge transfer in the dark and under light, and the smaller radius of arc in the spectrum indicate lower impedance and higher charge transfer. Thus, positive poling in dark and under light demonstrated lower impedance. In the MS (Figure 6-7(d)) measurement, the flat band potential was demonstrated to be higher in the negative poling photoanode than the no poling and positive poling photoanodes. The reason behind the different properties could be that a barrier is naturally created in the interface for negative poling, so it is believed that there is no charge transfer, even though there is no perfect polarization switching in the ferroelectric materials based layered structure. Therefore, the photocurrent in negative poling is nearly all in BiOI without any contribution of BTO photocurrent. Also, there is a high photovoltage in the positive poling photoanode, as shown in Figure 6-7(a) and (b) because of the long lifetime of photogenerated carriers due to charge separation. The higher impedance in the
negative poling photoanode is due to the barrier in the interface region. It is believed that the barrier was generated due to the creation of a virtual $p$-$n$ junction. The impedance between BiOI and the electrolyte is neglected because the same photoanode is used for positive and negative poling.

The virtual $p$-type is due to accumulated photogenerated holes at the interface, and this thus gives rise to the flat band potential, as shown in Figure 6-7(d). This kind of virtual $p$-$n$ junction with this band structure cannot contribute to charge separation, and the conduction band (CB) of BiOI still has lower potential than the CB of BTO, since otherwise anodic photocurrent can be observed. A schematic diagram has been drawn as shown in Figure 6-8 to illuminate the band structures for positive poling and negative poling. To test the claim that holes play an

![Figure 6-8 Schematic diagram of BTO/BiOI thin film and corresponding band structures for negative poling and positive poling photoanodes.](image)

![Figure 6-9 (a) Bar chart to show role electrons and holes in photodegradation (b) SEM image and EDS spectrum (inset) of BTO-BI-3 with photoreduction of Ag.](image)
absolutely key role in the decolouration process for pure BTO, a scavenger effect was created by adding sodium oxalate as a hole scavenger while added calcium iodate as an electron scavenger. The bar plot, as shown in Figure 6-9(a) demonstrates that the photocatalytic activity toward RhB photodegradation is affected with added scavengers. Firstly, with the electron scavenger, the photocatalytic activity is less affected with BTO compared with BTO-BI-3 demonstrating that holes are much more effective toward the photodegradation of RhB in BTO, whereas the electrons play this role in photodegradation with BTO-BI-3. Secondly, with the hole scavenger, the photocatalytic activity is much more affected with BTO compared with BTO-BI-3, implying the role of electrons in BTO-BI-3. As a result, the enhancement in photocatalytic activity of BTO-BI-3 occurs because of the contribution of the electrons in the reduction process, while in BTO, only holes play a role in photodegradation.

The high-performance activity of the heterojunction has a considerable effect on the band structure at the interface, and because the BTO and BiOI have a layered crystal structure and close band structures with a little higher CB of BTO than BiOI and only connection in the ab-plane (BiOI) with exposed [001] facets, as shown in Figure 6-2(i), which mean continue bonding Bi-O that it is possible for the pathways of electrons to cross from the Bi₂O₂ layer of BTO to the Bi₂O₂ layer of BiOI. Thus, the majority charge carriers (electrons) which are accumulated at the edge of BTO due to the positive polarization are transferred from the edge of BTO to the CB of BiOI. The transfer will stop when the Fermi levels are aligned. Consequently, salvation of the trapped electrons in the positively polarised regions has been achieved, and thus pathways are created for escape of the photoinduced electrons through BiOI. As can be seen in Figure 6-9(b). Although the charge transfer is single-type (electrons), but the photocatalytic activity is significantly enhanced. The schematic diagram in Figure 6-10 shows BiOI in contact with the
edges of BTO, and Figure 10 b shows the mechanism of the BTO/BiOI heterojunction, where it is clearly observed that the photoinduced electrons at the positive edges of BTO could be easily transferred to the CB of BiOI, and thus charge separation is achieved. Therefore, the photocatalyst performance has been enhanced.

6.4 Conclusion
We prepared single crystal plates of BTO from molten salts and then selectively deposited BiOI on the positive edges of BTO where there is positive polarization, and thus, a heterojunction has been achieved where electrons are transferred and injected into BiOI. Because band bending is generated at the interface between BTO and BiOI, the charge could be spatially separated. Significant enhancement of photodegradation has been obtained by this method compared with the conventional loading method. The complete photodegradation of RhB by the BTO-BI-3 sample requires 12 min under visible light, whereas phenol photodegradation is 47% in 60 min.

6.5 References


Chapter 7

Conclusions and Recombination for Future Work

7.1 Conclusions

This project included p-block photocatalyst-based internal electric field as shown in research works which are chapters four, five and six which were organized in three objectives: The first objective (chapter four) was investigated such as Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13}, by materials design and band engineering. Beside include internal electric generated from distortion SiO\textsubscript{4} chains inside crystal structure, Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13} possessed unique d\textsuperscript{10} and sp/p configurations in its electronic structure. This electronic structure promotes the generation, separation, and mobility of photo-induced charge carriers under visible-light illumination, which has been verified experimentally and theoretically. The experimentally results are consistent with calculation results that were demonstrated powerful oxidation potential toward organic dyes and phenol under visible light. This unique electronic structure and internal electric field originate from the p-block electronic configuration and distorted SiO\textsubscript{4} chains in Ag\textsubscript{10}Si\textsubscript{4}O\textsubscript{13}.

The second objective, photocatalytic activity of ferroelectric materials is highly influenced by the main direction of charge separation, originating from spontaneous polarization. In this work, unique bismuth silicate based zero-dimensional (0D)/two-dimensional (2D) heterogeneous nanostructures were successfully constructed. In contrast to either individual pristine phase, this heterogeneous structure exhibited much enhanced photocatalytic activity towards the degradation of Rhodamine B and phenol. The synergistic effects of high polarization in 2D ferroelectric Bi\textsubscript{2}SiO\textsubscript{5} nanosheets and the band bending at the 0D–2D interface of the heterostructures have been proved to accelerate the photoinduced charge separation and the movement of separated carriers to the interface, which further improves the photodegradation performance. This work provides a novel strategy for adjusting the photoinduced carrier transfer route in the ferroelectric materials and designing novel photocatalysts with ultrafast charge separation and large active surface area.

The third objective, ferroelectric-photocatalyst/photocatalyst heterojunctions have much attractive toward addressing challenging of photocatalytic performance, beside charge carrier separation by internal electric field, charge transfer has been further enhanced by heterojunction interface. In this work, the polarization-adsorption interaction which exists in ferroelectric materials was employed for successful deposition of BiOI on a specific surface of Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} in the dark at room temperature, where the positive polarized region of polarization is found. The crystal structure, morphology and composition of samples were confirmed by X-ray diffraction, field emission scanning electron microscopy and X-ray photoelectron spectroscopy respectively. The result shows higher activity by heterojunction, the reason behind enhancement activity was confirmed by firstly, the band structure contributed to photoelectrons transfer from Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} to BiOI, secondly, increase active site area of positive polar of Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}, thirdly, eliminate the screening layer which contribute impedance layer for charge transfer, fourthly, increase visible absorption.
In conclusion, the main points of these objective are contribution of internal electric field in photocatalytic activity and p-block compounds based ferroelectric materials. The internal electric field which provides by ferroelectric materials due to spontaneous polarization has provided driving force to enhance charge separation whereas p-block compounds are not only possess suitable band structure toward high oxidation potential but also possess high mobility charge carrier.

7.2 Recombination for Future Work

Although this thesis covers three compounds related to p-block based internal electric field but there are remains some work that would be benfit in future. The following some of these future works:

- Evaluate oxygen and hydrogen evolution for each component. The capability of redox potential for either water splitting or degradation organic pollutants strictly depends on the positions of CB and VB, The CB of Ag₁₀Si₄O₁₃ has shown lower negatively than reduction potential of H⁺/H₂, therefore, the hydrogen production by Ag₁₀Si₄O₁₃ is excluded, whereas BTO and BSO-HNS have shown higher negatively than reduction potential of H⁺/H₂, therefore, it is expected to produce H₂. The mineralization of dyes should be investigated by total organic carbon analysis removal measurement because decolorization of dye is not completely photodegradation.

- DFT calculation for a ferroelectric surface with interfacing with a semiconductor in certain face was hard to calculation with software, the exposed face with existence polarization in crystal structure interface with expose face for a material is complex to calculate.
Appendices

Appendix 1

List of publications


Conferences participating

1. 2018 International Symposium on Advanced Materials & Sustainable Technologies at QUT in Queensland

2. The 2nd International Symposium on Renewable Energy Technologies, Nov. 30 - Dec. 04, at UTS in Sydney