Photocatalytic hydrogen generation using two-phase anatase/brookite titanium dioxide nanostructures

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2015

Tay, Q. (2015). Photocatalytic hydrogen generation using two-phase anatase/brookite titanium dioxide nanostructures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62515>

<https://doi.org/10.32657/10356/62515>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**PHOTOCATALYTIC HYDROGEN GENERATION
USING TWO-PHASE ANATASE/BROOKITE
TITANIUM DIOXIDE NANOSTRUCTURES**

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A thesis submitted to the Nanyang Technological University in partial fulfilment of
the requirement for the degree of Doctor of Philosophy

2015

Abstract

Solar-driven water splitting with the use of photocatalyst is an attractive method to produce clean and sustainable hydrogen to meet the growing demand of energy. However, due to the challenges of fast photogenerated electron-hole recombination and limited absorption of the solar spectrum in photocatalytic water splitting, the solar to hydrogen energy conversion efficiency is limited. Hence, to enhance the hydrogen evolution, various approaches have been employed to enhance the charge separation by designing a heterojunction structure and to increase the light absorption using narrow band gap materials. The two strategies are shown to display synergistic effect when applied together.

Firstly, highly crystalline brookite and two-phase anatase/brookite TiO_2 nanostructures were synthesized via a simple hydrothermal method with titanium sulfide as the precursor in sodium hydroxide. The control of phase composition has been demonstrated via varying the sodium hydroxide concentration and by studying the TiO_2 phases formed with time-evolved hydrothermal reaction. Results have shown that anatase and brookite are formed from the transformation of sodium titanate. From the Mott-Schottky analysis, brookite phase is found to have a more cathodic conduction band potential than anatase phase which leads to higher hydrogen production via photocatalytic water splitting despite anatase having higher surface area. In addition, with two-phase anatase/brookite TiO_2 , the hydrogen production is further enhanced due to effective electron-hole separation as a result of charge transfer from brookite to anatase TiO_2 as evidenced from femtosecond transient absorption spectroscopy and photoluminescence spectroscopy. In comparison with the highly active two-phase commercial benchmark P25, the as-

synthesized two-phase anatase/brookite TiO_2 is 220 % more active when measured by the hydrogen yield per unit area of the photocatalyst surface.

To further enhance the hydrogen production, rGO was coupled with the two-phase anatase/brookite TiO_2 via chemical reduction of GO to further improve the charge separation. Graphene with its superior electrical conductivity can act as electron collector to further separate the photogenerated charge carriers in TiO_2 . Hydrogen production is enhanced with rGO-anatase/brookite TiO_2 mixture as compared to anatase/brookite TiO_2 . This is attributed to effective charge separation leading to the inhibition of photogenerated electron-hole recombination as evidenced from photoluminescence spectroscopy. Moreover, with rGO-anatase/brookite TiO_2 mixture, the hydrogen production is 2.3 times the amount of hydrogen produced with rGO-P25 mixture. This is due to the more cathodic conduction band potential of brookite than anatase and rutile TiO_2 which is energetically more favourable to reduce water to produce hydrogen.

To increase the solar to hydrogen conversion efficiency by enabling visible light harvesting, graphite-like carbon nitride ($\text{g-C}_3\text{N}_4$) which is visible light active was synthesized. Herein, a novel approach to tune the photophysical properties of $\text{g-C}_3\text{N}_4$ for efficient photocatalytic hydrogen production was developed by introducing hydrogen gas in the polycondensation reaction of $\text{g-C}_3\text{N}_4$ to create N vacancy and H substitution at N vacancy. With H doping in $\text{g-C}_3\text{N}_4$, the band gap is narrowed to 2.0 eV and produces open pore structures with threefold increase of surface area. The electronic structure calculations show that the band gap of H_2 treated $\text{g-C}_3\text{N}_4$ is narrowed by pushing the valence band to negative values as well as conduction band to positive values. Furthermore, partial density of states (PDOS) also suggests that defect induced states are

not localized on point defects but rather dispersed over neighboring sites which could help prevent the electron-hole recombination. Detailed chemical analysis using X-ray photoelectron spectroscopy and elemental analysis results confirm the stoichiometry corresponding to N vacancy and H substitution at N vacancy. With increased optical absorption in the visible range, higher surface area and open pore structure, the photocatalytic hydrogen production under visible light illumination is fivefold enhanced with g-C₃N₄ synthesized in pure H₂ [g-C₃N₄ (H₂)] as compared to g-C₃N₄ synthesized from the conventional method [g-C₃N₄ (air)].

Two-phase anatase/brookite TiO₂ was then coupled with the H₂ treated g-C₃N₄ to create a heterojunction. Results have shown that the number and type of TiO₂ phase in the g-C₃N₄/TiO₂ mixture greatly affect the hydrogen production. When H₂ treated g-C₃N₄ was coupled with two-phase anatase/brookite TiO₂, the hydrogen evolution is the highest as compared to H₂ treated g-C₃N₄ with single phase anatase, brookite, two-phase anatase/rutile and three-phase anatase/brookite/rutile. In addition, the hydrogen evolution is greatly enhanced with g-C₃N₄ (H₂)/TiO₂ mixture than g-C₃N₄ (air)/TiO₂ mixture as H₂ treated g-C₃N₄ has a smaller conduction band minimum offset with TiO₂ allowing faster electron transfer from g-C₃N₄ to TiO₂. With 20 wt% of two-phase anatase/brookite TiO₂ and 80 wt% of H₂ treated g-C₃N₄, hydrogen production under visible light is around 363 times (36.91 $\mu\text{mole h}^{-1} \text{ g}^{-1}$) that of normal g-C₃N₄. Our results demonstrate that H doping is a new strategy to improve the performance of g-C₃N₄ based photocatalysts.

In conclusions, modifying the electronic band structure of the material and inhibiting the fast electron-hole recombination play an important role in enhancing the hydrogen production via photocatalytic water splitting. In this thesis work, we developed novel

synthesis methods to synthesize brookite TiO_2 with more conduction band edge potential than anatase TiO_2 and modify the electronic band structure of the $\text{g-C}_3\text{N}_4$ with narrower band gap. In addition, to inhibit the fast electron-hole recombination, we created heterojunction for effective charge separation such as rGO with TiO_2 and $\text{g-C}_3\text{N}_4$ with TiO_2 . With increased optical absorption, higher surface area, energetically more favorable conduction band position and effective charge separation, desired solar water splitting system could be achieved.

Acknowledgements

I would like to express my heartfelt appreciation and sincere gratitude to the following people who have offered his/her guidance, advice, support and encouragement to me during my PhD study.

Firstly, I would like to express my deepest gratitude to my supervisor, Prof. Chen Zhong, for giving me the opportunity to pursue my graduate studies under his supervision. I truly appreciate his invaluable guidance, advice, encouragement and continuous support to allow me to explore the research areas that I am interested in. He has given me a very rewarding and lasting experience throughout the entire course of my graduate studies.

I would like to extend my gratitude to Dr. Martin Schreyer and Dr. Stevin Snellius Pramana for their advice on Rietveld refinements of XRD results, Dr. Tay Yee Yan on his guidance on TEM, Dr. Liu Xinfeng for his help in the femtosecond transient absorption spectroscopy, Dr. Chen Shi and Mr. Ng Chin Fan for their help and advice on the XPS analysis, Dr. Wang Xing Hui for his help in heat treating the g-C₃N₄ sample in pure H₂, Dr. Hong Jindui for his help in the elemental analysis of the g-C₃N₄ samples, Dr. Kanhere Pushkar Dilip, my group member, Dr. Sudip Chakraborty and Prof. Rajeev Ahuja from Uppsala University for the DFT based electronic structure calculations of the g-C₃N₄ samples. I would also like to thank Prof. Sum Tze Chien, Prof. Alfred Huan Cheng Hon, Prof. Zhang Qing and Prof. Xu Rong for allowing me to use their facilities. In addition, many thanks to my group members, Dr. Tang Yuxin, Dr. Gong Dangguo, Dr. Wang Danping, Dr. Zhang Yanyan, Mr. Jeffrey Ho, Miss Qi Huan, Mr. Vinod Kumar s/o

Murugan, Mr. Jiang Zhelong, Mr. Deng Jiyang and Miss Linda Lim Ying Wen for their technical advice, support and encouragement.

I would like to express my gratitude to Nanyang Technological University for supporting my doctoral degree with Nanyang President's Graduate Scholarship. Special thanks to my family and friends for their emotional support and encouragement. Last but not least, I would like to thank the people whose names are not mentioned, whom have contributed directly and indirectly to this work.

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Chapter 1: Introduction

1.1 World Energy: Increasing Demand and Challenges

Energy demand by humanity continues to rise and the world energy consumption is projected to increase from 524 quadrillion Btu in 2010 to 820 quadrillion Btu in 2040, an increase of 56 % over 30 years time as shown in Figure 1.1 ¹. The increase in world energy consumption is driven by the increasing human population and the industrialization of developing countries. According to official United Nation population estimates (Figure 1.2), the total world population in mid-2013 was 7.2 billion which was 648 million more than in 2005 or an average gain of 81 million persons per year ². By 2100, the world population is projected to increase to 10.9 billion. The world energy supply mainly comes from fossil fuels — over 80 % of energy is produced from the burning of fossil fuels. In 2011, 37 % of energy supply comes from petroleum, 26% from natural gas and 20 % from coal (Figure 1.3). Together, these three fossil fuels made up 83% of the world energy supply ¹. With the increasing demand of energy, this leads to more extraction of the fossil fuels and hence lesser supply of fossil fuels as the depletion rate is much faster than the replenish rate. According to M. King Hubbert, a well known U.S. geologist working for Shell Oil, oil supply will reach a maximum point in time known as peak oil where the rate of petroleum extraction is at maximum and then after the rate of production will enter terminal decline ³. Colin Campbell, a petroleum geologist, proposed that the peak oil would occur at 2007 and the oil and gas production would decrease rapidly as shown in Figure 1.4 ^{4,5}.

Figure 1.1 World energy consumption from 1990 to 2010 and projected world energy consumption from 2011 to 2040 in quadrillion Btu ¹. Source: U.S. Energy Information Administration (International Energy Outlook 2013).

Figure 1.2 Total world population by major areas. The world population is projected to increase to 10.9 billion by 2100 ². Source: World Population Prospects: The 2012 Revision, Department of Economic and Social Affairs, © 2012 United Nations. Reprinted with the permission of the United Nations.

Figure 1.3 World energy consumption fuel shares in 2010 with 83 % from fossil fuels ¹.

Source: U.S. Energy Information Administration (International Energy Outlook 2013).

Figure 1.4 World Oil Production Forecast with peak oil occurring at 2007 ⁴. Source:

APSO Newsletter #89.

In addition, the use of fossil fuels has led to severe environmental issues such as emission of carbon dioxide (CO₂), depletion of the ozone layer and global warming. Carbon dioxide emissions are expected to increase from 31.2 billion metric tons in 2010 to 36.4 billion metric tons in 2020 and 45.5 billion metric tons in 2040, an increase of 46 percent over the projection period as shown in Figure 1.5 ¹. As a result, with the depleting supply of fossil fuels and more severe environmental issues, it is imperative to develop alternative energy which is renewable and environment friendly.

Figure 1.5 Carbon dioxide emissions from 1990 to 2010 and projected to increase 46 % at year 2040 (billion metric tons) ¹. Source: U.S. Energy Information Administration (International Energy Outlook 2013).

1.2 The Hydrogen Economy

In year 1965, the idea of “hydrogen economy” or large-scale hydrogen energy system was first expressed by E. Justi in his book “Conduction mechanisms and energy conversion” ⁶. In 1990, the world’s first solar-powered hydrogen production plant became operational at Solar-Wasserstoff-Bayern, a research and testing facility in southern Germany ⁷. Over the past few decades, interest in hydrogen to replace fossil fuels has surged as it is abundant, clean and renewable. Hydrogen is a high density energy carrier with a high gravimetric energy density of 140 kJ g⁻¹ at 35 MPa compared to others such as 50 kJ g⁻¹ for liquid fuels ⁸. Hydrogen is one of the most abundant elements on the earth which exists in the form of water and hydrocarbon. When hydrogen is combined with oxygen in fuel cell, chemical energy of the hydrogen fuel is converted to electrical energy with only water and heat as the byproducts with no harmful gases given out ($2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$; $\Delta G = -123 \text{ kJ mol}^{-1}$).

Although hydrogen is an attractive alternative to replace fossil fuels, hydrogen economy is still in the early stages of development and faces many challenges. One of the major challenges is that a cost-effective hydrogen production strategy with low greenhouse gas emission has yet to be developed ⁹. Even though hydrogen is highly abundant on earth, it is bonded with other element in water or hydrocarbons which has to be chemically transformed to produce hydrogen. Currently, hydrogen is produced from natural gas by a steam-methane reformation method (SMR) which accounts for 95% and 48% of all hydrogen produced in the United States and in the world ¹⁰. In this method, natural gas which has methane as the major component reacts with steam over a catalyst bed at high temperature and pressure to form a mixture of hydrogen and carbon

monoxide ($\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$; $\Delta H = 206.1 \text{ kJ mol}^{-1}$). The carbon monoxide will further reacts with additional steam to form carbon dioxide and more hydrogen ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$; $\Delta H = -41.1 \text{ kJ mol}^{-1}$)⁷. In this high temperature conversion of methane to hydrogen, it involves the emission of carbon dioxide and carbon monoxide which is not environmentally friendly. Hence, we must produce hydrogen from zero-carbon and renewable sources, such as water in order for the hydrogen economy to be beneficial.

1.3 From Natural Photosynthesis to Artificial Photosynthesis

An attractive alternative to produce hydrogen from non-fossil resources is through solar-driven water splitting which is demonstrated in the photosynthesis process by the green plants. In the nature world, plant is able to absorb sunlight and convert the solar energy into chemical energy through the process of photosynthesis. When light is absorbed by the plant, the radiant energy is transferred to the photosystem II (PSII) reaction center which causes the electrons of chlorophylls of the reaction center to be excited. These excited electron are then transferred through the electron transport chain to the photosystem I (PSI) reaction center. To be reduced back to ground state, the electron-deficient photosystem II reaction center receives electrons from the oxidation reaction of water (equation 1.1). Subsequently, the electron flow from PSII to PSI shuttle the protons formed from the oxidation of water to nicotinamide adenine dinucleotide phosphate-oxidase (NADP^+) in PSI and produce hydrogen in the form of NADPH (equation 1.2). During this process, the energy of sunlight is stored by the plants in the form of chemical bonding^{11, 12}.

Figure 1.6 Schematic of photosynthesis process in green plants involving three main steps which are (1) light harvesting, (2) charge separation and (3) photocatalytic reaction to produce nature's form of hydrogen (NADPH) ¹¹.

Based on the study of the natural photosynthesis process, the photosynthesis process can be summarized into three main steps which are (1) harvesting of sunlight, (2) separation of electron-hole pairs and (3) the photocatalytic reaction to produce nature's form of hydrogen (NADPH) as shown in Figure 1.6. This provides a blueprint for scientists to design solar water splitting systems to convert solar energy into chemical

fuels. Analogous to the nature photosynthesis, artificial photosynthesis is achievable with the use of semiconductor photocatalyst to produce hydrogen and oxygen from the water splitting under solar illumination and the first hydrogen production through solar-driven water splitting was discovered by Fujishima and Honda over titania (TiO_2) photoanode under the irradiation of Ultra-Violet (UV) light in 1972¹³. Since its discovery, extensive research has been carried out on solar-driven water splitting as it is a renewable and clean method to produce hydrogen with zero emission of greenhouse gases. Water is abundantly available on earth and hydrogen produced from solar-driven water splitting can be combined with oxygen in fuel cells to produce electrical energy and giving back water as the by-products, making it a renewable cycle as shown in Figure 1.7. Moreover, the cost of hydrogen production via solar-driven water splitting is relatively low as the use of solar energy allows sustainable energy generation at low cost and most of photocatalysts used are oxide-based semiconductors which are cheap and ample in availability. As a result, solar-driven water splitting is one of the promising methods to produce hydrogen as the next generation fuel.

Figure 1.7 Schematic of solar hydrogen cycle where hydrogen produced from solar-driven water splitting is used to react with oxygen to produce electrical energy and giving back water as the by-products.

1.4 Solar Hydrogen Production via Water Splitting

Solar hydrogen production via water splitting with the use of semiconductors photocatalysts as light absorber and energy converter could be achieved by two main methods: photo-electrochemical (PEC) water splitting and particulate photocatalytic water splitting. Both of these two methods involve working under light irradiation conditions and generating electron-hole pairs for redox reactions in aqueous solution.

1.4.1 Photo-Electrochemical Water Splitting

In photo-electrochemical water splitting, a photoactive semiconductor electrode is employed as the working electrode. Typically, the working electrode is made up of a photoactive semiconductor thin film deposited or grown on a conducting substrate. Both the photoactive semiconductor electrode and counter electrode made of either metal or semiconductor are immersed in an electrolyte. When light which has energy greater than the band gap of the semiconductor is irradiated at the semiconductor electrode, electron-hole pairs are generated and separated in the space charge region between electrode and electrolyte. At the semiconductor electrode-electrolyte interface, the photogenerated holes will oxidize water to form oxygen gas while the photogenerated electrons are transferred through the connecting wire to the counter electrode and reduce protons at the counter electrode-electrolyte interface to form hydrogen gas as shown in Figure 1.8¹⁴. By applying a bias, due to the presence of the electric field, the recombination of the photogenerated electron-hole pairs can be inhibited and thus enhancing the water splitting activity.

Figure 1.8 Schematic representation of a photo-electrochemical cell (PEC).

1.4.2 Particulate Photocatalytic Water Splitting

For photocatalytic water splitting, particulate photocatalysts are suspended in the water under light irradiation. Typically, sacrificial agent like methanol for hydrogen gas production or silver nitrate for oxygen gas evolution is added into the suspension to further enhance the production. Solar-driven water splitting with particulate photocatalyst is a simpler and cheaper method as compared to PEC and it is more suitable for large scale applications. Thus, in this study, it will be focused on photocatalytic water splitting with particulate photocatalysts.

The mechanism of photocatalytic water splitting by semiconductor particulate consists of three main steps: (1) absorption of photons of suitable energy to generate electron-hole pairs, (2) separation and transportation of the photogenerated electrons and holes and (3) chemical reaction between charge carriers and surface species (Figure 1.9)¹⁵. When light in term of photons is irradiated on a semiconductor where the photon has energy equal or higher than the band gap, the electrons in the valence band will receive energy from the photon and be excited to the conduction band (CB) leaving holes in the valence band (VB) and hence generating electron-hole pairs. However, these electron-hole pairs are able to recombine in bulk or on the semiconductor surface within a short time. Thus, only those holes and electrons that migrate to the surface of the semiconductor without recombination will be able to oxidize water to oxygen as shown in equation 1.3 and reduce the hydrogen ions to hydrogen gas as shown in reaction equation 1.4.

Figure 1.9 Mechanism of photocatalytic water splitting for hydrogen production ¹⁵.

1.5 Solar Hydrogen Generation Challenges and Solutions

In order to produce hydrogen via photocatalytic water splitting, there are two prerequisites on the band gap and band edge potentials of the semiconductor photocatalyst which have to be fulfilled. Firstly, under standard conditions, the free energy change for conversion of one molecule of H_2O to H_2 and $\frac{1}{2} \text{O}_2$ is $\Delta G = 237.2 \text{ kJ mol}^{-1}$ which corresponds to $\Delta E^\circ = 1.23 \text{ V}$ per electron transferred according to the Nernst equation ¹⁶. Thus, band gap energy of more than 1.23 eV is required for water splitting. However, studies have shown that much higher band gap energy of 1.6 eV is required for photocatalytic water splitting due to the energy losses associated with the

overpotentials required for hydrogen and oxygen production^{17, 18}. Furthermore, electrochemical potential of the holes in the valence band has to be more positive than the redox potential of O_2/H_2O (+1.23 V vs. NHE) in order to oxidize water to oxygen and for hydrogen production, the electrons in the conduction need to have potential more negative than the redox potential of H^+/H_2 (0 V vs. NHE). Hence, the band edge potentials of the semiconductor play an important role in photocatalytic water splitting.

Figure 1.10 shows the band gap level of some of the semiconductors with respect to the redox potential of water oxidation and hydrogen production¹⁸. Theoretically, semiconductors that have band gap energy of at least 1.23 eV and suitable band edge positions for reduction/oxidation of water can be used as photocatalyst for hydrogen production via water splitting but most of the non-oxide semiconductors such as CdS and SiC are not chemically stable or they undergo self-oxidation under illumination¹⁹. On the other hand, most of the oxide semiconductors which fulfilled the requirements such as Ti-based oxides (for example: TiO_2 ^{20, 21}, $Na_2Ti_3O_7$ ^{22, 23} and $SrTiO_3$ ^{24, 25}), Ta-based oxides (for example: Ta_2O_5 ^{26, 27} and $KTaO_3$ ^{28, 29}) and Nb-based oxides (for example: Nb_2O_5 ^{30, 31} and $K_4Nb_6O_{17}$ ^{32, 33}) exhibit superior photochemical stability in aqueous solution. However, due to its wide band gap, most of these oxide semiconductors are only active to UV light which is only 5 % of the solar spectrum. For example, anatase TiO_2 has band gap of 3.2 eV (387.5 nm) and both Ta_2O_5 and Nb_2O_5 have band gap energy of 3.4 eV (364.7 nm)⁹ and thus these oxide semiconductors are only able to absorb UV light and results in low solar to hydrogen conversion efficiency.

Figure 1.10 Band gap level of various semiconductors relative to redox potential of water

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In addition, one of another challenges faced in the generation of solar hydrogen is the fast recombination of the electron-hole pairs in bulk and/or on the surface. When the photogenerated electrons and holes recombine, the electrons and holes will not be able to reduce protons to form hydrogen gas and oxidize water to form oxygen gas respectively. As a result, the photocatalytic activity is limited by the recombination of the electron-hole pairs. Therefore, to enhance the solar to hydrogen conversion efficiency, the photocatalyst has to be photochemically stable, visible light active and has good photogenerated charge separation so as to inhibit electron-hole pair recombination. As a result, extensive research has been carried out to counter these challenges.

In the following sections, detailed studies aiming to counter these challenges are reviewed.

1.5.1 Enhancement of Hydrogen Production by Addition of Sacrificial Agents

In photocatalytic water splitting, due to the fast recombination of the photogenerated electrons and holes and the thermodynamically favorable backward reaction of H_2 and O_2 to form H_2O , pure water splitting for hydrogen production is difficult to achieve. In addition, oxidation of water is a much slower process than hydrogen evolution due to the more complex process of the requiring four holes to produce oxygen from two water molecules as compared to the much simpler two-electron hydrogen evolution³⁴⁻³⁶. Thus, in order to smoothen the progress of the water oxidation, sacrificial agent, hole scavenger or electron donor, is added to prevent the electron-hole recombination. Once the holes are scavenged from the photocatalyst surface, the longer decay time of the surface electrons will facilitate the reduction of protons to form hydrogen³⁶.

Organic compounds are widely used as hole scavengers for photocatalytic water splitting as they can be oxidized by photogenerated holes and reduce the probability of electron-hole recombination. Several studies have been investigated on different hydrocarbon hole scavengers to improve the hydrogen production and methanol among the alcohol series is found to be the most effective hole scavenger as compared to organic acids and ketones³⁶⁻³⁹. This is because of organic acids and ketone higher polarity, more stable electronic configuration and longer carbon-carbon chain elongation. With increase in chain elongation and complexity, the extent of carbon-to-carbon bond breaking decreases which enhances the steric hindrance in the molecule³⁶.

Moreover, with the addition of sacrificial agents, it can help to prevent the photocorrosion of non-oxide semiconductors such as CdS. As mentioned earlier, CdS photocatalyst is chemically unstable as it can be easily photo-corroded as follows:

Thus, sacrificial agents such as Na_2S and Na_2SO_3 are added in which the S^{2-} ions will react with two holes to form S and the SO_3^{2-} ions will react with S to form $\text{S}_2\text{O}_3^{2-}$ to prevent any detrimental deposition onto CdS. As a result, photocorrosion of CdS is prevented^{19, 39-41} and photocatalytic activity is enhanced.

1.5.2 Enhancement of Hydrogen Production by Cocatalyst Loading

To inhibit the recombination of photogenerated electron-hole pairs, loading of cocatalyst on the photocatalyst surface is an effective method to separate the electron-hole pairs in order to enhance the hydrogen production. Noble metals such as Pt, Au and Pd have been reported as effective cocatalysts for photocatalytic water splitting to produce hydrogen^{42, 43}. As the Fermi energy level of the noble metal is always lower than the semiconductor photocatalyst, the photogenerated electrons will migrate from the conduction band of the semiconductor photocatalyst to the noble metal particles loaded on the surface of the photocatalyst. Meanwhile, the photogenerated holes will remain on the host photocatalyst as shown in Figure 1.11. As a result, the photogenerated electrons and holes are separated and the electron-hole pair recombination is greatly reduced.

Subsequently, the separated holes and electrons will be able to effectively oxidize water and reduce protons to form hydrogen gas respectively ⁹.

Figure 1.11 Processes of charge transfer between host photocatalyst and cocatalyst ⁹.

Studies have shown that Pt loading prepared by photodeposition is the most effective cocatalyst as compared to Au, Pd and as well as other loading methods such as deposition-precipitation and impregnation. Sakthivel et al. investigated the photooxidation of organic dye with Pt, Au and Pd loaded TiO₂ photocatalyst and it was found that Pt and Au loaded on TiO₂ photocatalysts were more effective than Pd-loaded TiO₂ due to more suitable electron affinity and work function of Pt and Au ^{19, 42}. In addition, Bamwenda et al. investigated the amount of hydrogen produced by Au-loaded TiO₂ and Pt-loaded TiO₂ photocatalyst prepared by photodeposition, deposition-precipitation and impregnation methods. It was found that loading of Pt on TiO₂ produces higher amount of hydrogen as compared to Au-loaded TiO₂. Moreover, loading method of photodeposition was found to work better than deposition-precipitation and

impregnation methods which might be explained by the better contact with TiO_2 active sites for the photodeposition method ^{19, 43}. Currently, Pt co-catalyst has been widely used and recognized as it has shown great enhancement of hydrogen production.

1.5.3 Enhancement of Hydrogen Production via Visible Light Harvesting

Among all approaches to modify the wide band gap photocatalysts for visible light harvesting, it could be classified into two categories: (1) metal and/or non-metal ions doping to create impurity levels in the forbidden band to narrow the band gap and (2) coupling with a secondary component which is visible light active.

1.5.3.1 Doping of Metal/Non-Metal Ions

To develop visible light driven photocatalyst, one of the most effective methods is to create additional electronic states in the band gap through metal ions doping. Depending on the nature of the dopant, either an acceptor level above the valence band or a donor level below the conduction is formed in the forbidden band as shown in Figure 1.12 ⁹. These newly formed electronic states will narrow the effective band gap making the photocatalysts visible light active. Over the years, modification of wide band gap photocatalysts to make it visible light active using metal ion doping was extensively explored. In 1982, Borgarello et al. reported Cr^{5+} doped TiO_2 could produce hydrogen and oxygen under visible light illumination in the range of 400 to 550 nm ⁴⁴. Since then, many different metal ions such as V ^{45, 46}, Ni ^{47, 48}, Cr ^{44, 49}, Mo ^{50, 51}, Fe ^{52, 53}, Sn ^{54, 55} and

Mn^{56, 57} have been doped into TiO₂ to improve the visible-light absorption and photocatalytic activities.

Figure 1.12 a) Acceptor level and b) donor level formed by metal ion doping⁹.

Similar to metal ions doping, doping of non-metal ions can narrow the band gap of the semiconductor photocatalysts by shifting the valence band edge upward as shown in Figure 1.13⁹. Studies have shown that by chemical doping of non-metal ion such as N⁵⁸, S⁵⁹ or C⁶⁰, it could fine tune the band structure of TiO₂ to have lower band gap so as to be visible light active. Asahi et al. investigated the substitutional doping contents of C, N, P or S for O in anatase TiO₂ by using full-potential linearized augmented plane wave (FLAPW) method to calculate the electronic band structures of anatase TiO₂ with different substitutional dopants. They found that doping of N was the most effective as mixing of p states of N with 2p states of O could shift the valence band of TiO₂ upwards

and thus narrowing the band gap of TiO_2 ⁶¹. Although doping with S shows similar band gap narrowing, the ionic radius of S is too large to be incorporated into the TiO_2 crystal as evidenced by a much larger formation energy required for the substitution of S than that required for the substitution of N⁶¹. Furthermore, doping of C or P were found to be less effective as the introduced states were too deep for the photogenerated charge carriers to be transferred to the surface of the catalyst.

Figure 1.13 New valence band formation by doping of non-metal ions⁹.

Although doping of metal and/or non-metal ions can enhance visible light absorption, it can have adverse effects on the photocatalytic activity. Introduction of aliovalent dopant can cause ionic charge imbalance in the lattice and to compensate for the charge imbalance, native point defects are formed. These defects can act as recombination centers and results in electron-hole recombination. In addition, metal ions should be

doped near the surface of photocatalysts for better charge transferring. In case of deep doping, the metal ions are likely to behave as recombination centers. In comparison to non-metal ions doping, metal ions doping is more likely to form recombination centers and therefore it is less effective in enhancing the photocatalytic activity⁹. As a result, to minimize the adverse effects of doping, it is important to choose suitable dopants with suitable doping content and depth for the development of photocatalysts to be visible light active and as well as having high photocatalytic activities.

1.5.3.2 Coupled Water-Splitting System

Other than narrowing the band gap of the semiconductor photocatalyst to absorb visible light, another method for visible light harvesting is to couple the wide band gap semiconductor with secondary component which is visible light active. These secondary components include narrow band gap semiconductors, visible light absorbing dye, plasmonic metal nanostructures and so on.

One simple way to modify the wide band gap semiconductor for visible light harvesting is to couple the wide band gap semiconductor with another narrow band gap semiconductor which is visible light active. In order to achieve efficient solar hydrogen generation via water splitting, there are several requirements to be fulfilled: (1) The narrow band gap semiconductor has to have band gap narrow enough to absorb visible light in the solar spectrum and has high absorption coefficient in the visible light region. (2) Suitable band edge positions for reduction and/or oxidation of water such as the wide band gap semiconductor conduction band potential has to be more cathodic than the

potential of water reduction in order to generate hydrogen. (3) The conduction band potential of narrow band gap semiconductor has to be more cathodic than the conduction band potential of wide band gap semiconductor for effective charge transfer and separation. One example of coupling narrow band gap semiconductor with wide band gap semiconductor for hydrogen generation under visible light irradiation would be coupling cadmium sulfide (CdS) with TiO_2 . CdS has a narrow band gap of 2.4 eV and high absorption coefficient in the visible light region ⁶². In addition, the conduction band position of CdS is 0.5 eV more negative than conduction band position of TiO_2 and thus the electrons in CdS can be transferred to TiO_2 under visible light illumination leading to improvement of charge separation efficiency as shown is Figure 1.14 ^{62, 63}. Therefore, by coupling CdS with TiO_2 , it could enhance the hydrogen generation via photocatalytic water splitting under visible light illumination.

Figure 1.14 Illustration of the electron transfer from CdS to TiO_2 ⁶³.

Dye sensitization is another widely used approach to enable the visible-light harvesting of wide band gap semiconductors. Ever since the invention of dye-sensitized solar cell (DSSC) by Brian O'Regan and Michael Grätzel in 1991⁶⁴, DSSC has received great attention due to its low cost, good stability and high device efficiency⁹. In DSSC, it involves the excitation of dye under light illumination and the charge transfer from the dye to the semiconductor. Similarly, in photocatalytic water splitting, the electrons in the excited dye are injected to the conduction band of the semiconductors to reduce water to form hydrogen under visible light illumination. Thus, some of dyes which have redox properties and are sensitive to visible light can be used in both solar cells and photocatalytic systems¹⁹.

The basic principle of dye-sensitized photocatalytic water splitting to generate hydrogen under visible light irradiation is illustrated in Figure 1.15. Under visible light irradiation, the dye is photoexcited and the photogenerated electrons are injected from the dye to the conduction band of the semiconductor to reduce water to produce hydrogen. In order to regenerate the dye, sacrificial electron donor (Ethylenediaminetetraacetic acid, EDTA) or non-sacrificial donor (iodide, I⁻) is added to sustain the reaction cycle whereby the oxidized dye molecules are reduced by accepting electrons from the electron donor.

Figure 1.15 Basic principle of dye-sensitized photocatalytic water splitting for hydrogen generation under visible light irradiation ¹⁹.

A large varieties of dyes, such as $\text{Ru}(\text{bpy})_3^{2+}$ ⁶⁵, $\text{Ru}(\text{dcbpy})_3$ ⁶⁶, $\text{Ru}(\text{bpym})_3^{2+}$ ⁶⁷, $\text{Ru}(\text{dcbpy})_2(\text{dpq})^{2+}$ ⁶⁸, and $\text{c-(or p)-Ru}(\text{bpy})_3^{2+}$ ⁶⁹ are used for dye-sensitized photocatalytic water splitting to generate hydrogen. Although dye sensitization is an effective strategy to enable visible light harvesting, these dyes may suffer from severe degradation. Thus, it is essential to develop stable and highly efficient photocatalytic systems.

In recent years, plasmon-enhanced water splitting on composite photocatalysts containing semiconductor and plasmonic-metal nanostructures (mainly noble metals such as gold and silver) has received great attention as it shows significant promise in harvesting and conversion of solar energy. Surface plasmon resonance (SPR) is an optical phenomena generated by the strong interaction between plasmonic-metal nanostructures and resonant photons ⁷⁰. SPR can be described as the resonant photon-induced collective

oscillation of valence electrons of the metallic nanostructure which is generated when the frequency of photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei ⁷¹. Studies have shown that the highest rate of photocatalytic activity enhancements were observed at the wavelengths corresponding to the metal SPR ⁷²⁻⁷⁴ and the SPR intensity and resonant wavelength are dependent on the nature, size and shape of metallic nanostructures ⁷⁴⁻⁷⁶. Thus, by controlling the composition, shape and/or size of plasmonic nanostructures, highest enhancement of photocatalytic activity could be achieved. Basically, there are three types of mechanisms where the SPR can enhance the concentration of charge carriers and the rates of photocatalytic reaction. These three mechanisms will be discussed below.

One of the mechanisms is the direct injection of charge carriers from the excited plasmonic-metal nanostructures into the semiconductor surface. This mechanism is very much similar to the dye sensitization mechanism where the metallic nanostructure serve as the dye sensitizer which absorbs the resonant photons and transfers the excited electrons formed in the process of SPR excitation to the nearby semiconductor as shown in Figure 1.16 ⁷¹. These transferred electrons will subsequently be consumed through water reduction reaction to generate hydrogen. Due to the excellent mobility of charge carriers and high absorption cross-sections, plasmonic-metal nanostructures are more promising sensitizers than dye sensitizers as under resonance conditions, the cross section of plasmonic nanostructures is 10^5 times larger than the cross-section of typical dye-sensitizer molecules ^{71, 77}. In addition, by changing the size or shape of the metallic nanostructures, the resonance wavelength can be modified which suggests that the entire solar spectrum can be exploited with the use of plasmonic-metal sensitizers.

Figure 1.16 Mechanism of SPR-induced charge transfer from plasmonic metal to semiconductor to generate hydrogen. (i) Plasmonic metal electrons which are near the metal Fermi level, E_f are excited to surface plasmon (SP) states. (ii) Electrons transfer from SP states to the conduction band of nearby semiconductor particle. (iii) The transferred electrons in the conduction band of the semiconductor reduce water to generate hydrogen ⁷¹.

Even if the plasmonic metal is not in direct contact with the semiconductor and are separated from each other by thin and non-conductive spacer preventing direct charge exchange, radiative energy transfer from the metal SPR to the semiconductor can occur through near-field electromagnetic mechanism ⁷¹. The near-field electromagnetic mechanism is based on the interaction of strong SPR-induced electric fields localized

nearby the metallic nanostructure with the semiconductor and the role of the photoexcited plasmonic nanostructures is to be nanosized concentrators that can amplify the local light intensity. When a semiconductor is near the photoexcited plasmonic-metal nanostructure, the strong SPR-induced electric field of the metal nanostructure causes the semiconductor to be excited and forms electron-hole pairs where the rate of formation is proportional to the local intensity of the electric field (more specifically $|E|^2$)^{78, 79}. However, the intensity of this electric field is spatially non-homogenous which causes the rate of induced electron-hole pair formation to be highest on the surface of the semiconductor as it is closest to the plasmonic nanostructure. As a result, these electron-hole pairs formed on the surface of the semiconductor can be readily separated under the influence of surface potential leading to effective charge separation and less electron-hole pair recombination. Moreover, these surface electrons and holes can be easily migrated with the shortest distance to the semiconductor/liquid interface to reduce and oxidize water respectively. Hence, the photocatalytic activity is greatly enhanced with lower probability of electron-hole recombination.

Another mechanism of radiative energy transfer from the metal SPR to the semiconductor which is in nearby contact with each other is through resonant photon-scattering. When the plasmonic nanostructure is larger than 50 nm in diameter, the metal SPR is accompanied by an efficient scattering of resonant photons^{80, 81}. Due to the scattering of photons by plasmonic nanostructures, the average photon path length in plasmonic nanostructures and semiconductor composites increases which leads to a higher rate of electron-hole pair formation in the semiconductor and thus higher photocatalytic activity as shown in Figure 1.17⁷¹.

Figure 1.17 Schematic illustrating resonant photon-scattering mechanism. The average path length of the photons is increased in the composite formed by the addition of optically excited plasmonic metal nanostructures with semiconductor⁷¹.

Hence, by coupling the wide band gap semiconductor with secondary component which is visible light active, visible light harvesting could be achieved. In addition, in some cases, the photocatalytic activities are further enhanced due to effective charge separation caused by the transfer of charge carriers from the secondary components to the wide band gap semiconductors.

1.6 Summary

In summary, due to the depletion of fossil fuels, increasing human population and more severe environmental problems, there is an urgent need to develop alternative fuels. Hydrogen is a promising next generation fuel as it is abundant, clean and renewable. An attractive method to produce hydrogen from non-fossil resources is through solar-driven water splitting as it is a renewable and clean method with zero emission of greenhouse gases. To produce hydrogen via photocatalytic water splitting, there are two prerequisites on the band gap and band edge potentials of the semiconductor photocatalyst which have to be fulfilled. The semiconductor photocatalyst has to have band gap energy of more than 1.23 eV and has suitable band edge positions for reduction/oxidation of water. Although metal oxides that fulfilled the electronic band structure requirements are ideal photocatalysts for photocatalytic water splitting as it is photochemically stable, most of the metal oxides are only active to UV light which is only 5 % of the solar spectrum due to its wide band gap. As a result, it limits the solar to hydrogen conversion efficiency. In addition, due to the fast recombination of the photogenerated electron-hole in bulk and/or on the surface of the semiconductor photocatalyst, the water reduction reaction to produce hydrogen is limited.

To counter these challenges in solar-driven water splitting to produce hydrogen, addition of sacrificial agent and cocatalyst loading are used to inhibit the recombination of photogenerated electron-hole pairs. For visible light harvesting, wide band gap semiconductors are modified via metal and/or non-metal ions doping to create impurity levels in the forbidden band so as to narrow the band gap. Secondary component which is

visible light active can be coupled with the wide band gap semiconductor in order to generate hydrogen via photocatalytic water splitting under visible light irradiation. These secondary components can be narrow band gap semiconductors, visible light absorbing dye and plasmonic metal nanostructures. In addition, in the coupled/composite system, the photocatalytic activity is further enhanced due to the effective charge separation caused by the transfer of charge carriers from the secondary component to the wide band gap semiconductor.

Therefore, to realize the idea of hydrogen economy and satisfying the market discipline of cost, reliability and performance, continuous efforts to design and develop solar-driven water splitting systems with high solar to hydrogen conversion and low probability of electron-hole recombination is required. Moreover, to reduce cost, the use of cheap and earth-abundant semiconducting materials should be employed. In addition, other than focusing on enhancing the hydrogen production, extensive research on innovative hydrogen storage methods and fuel cell technologies are very much needed. Currently, the traditional hydrogen storage method involves storing hydrogen in cylinders or tanks of liquid and high-pressure gas. Storage as liquid hydrogen results in severe energy costs as up to 40% of its energy content can be lost to liquefaction. Therefore, to replace the traditional storage method, hydrogen can be stored and released in portable solid-state media and fuel cells that convert hydrogen to electrical power. In addition, to achieve higher efficiency of fuel cell, coupling fuel cells to electric motors to convert chemical energy of hydrogen to mechanical work without heat as intermediary can increase the fuel cell efficiency from 60 % to 90 %⁸².

1.7 Research Scope and Objectives

In this project, to counter the challenge of fast electron-hole recombination faced in photocatalytic water splitting and to enhance the hydrogen production, we synthesized two-phase anatase/brookite TiO_2 nanostructures. TiO_2 has been a popular candidate as the photocatalyst for water splitting. Majority of the reported research on TiO_2 for photocatalytic water splitting was on anatase and/or rutile TiO_2 . On the other hand, brookite TiO_2 is rarely studied due to the difficulty in synthesizing as it is furthest away from equilibrium under ambient conditions⁸³. However, it was reported that brookite nanocrystals have higher photocatalytic activities as compared to rutile and anatase^{84, 85}. In this study, TiO_2 in the form of pure anatase nanoparticles, pure brookite nanoplates and two-phase anatase/brookite mixture were synthesized using titanium sulfide in alkaline sodium hydroxide medium via a simple hydrothermal method. The photocatalytic activities of the as-synthesized TiO_2 nanostructures were evaluated by measuring the hydrogen generation via photocatalytic water splitting under UV light. To determine the conduction band edge potential of the brookite phase and the anatase phase, Mott-Schottky analysis was carried out. Femtosecond transient absorption spectroscopy and photoluminescence spectroscopy were employed to determine the charge carrier lifetime

Moreover, to further inhibit the electron-hole recombination, the as-synthesized anatase/brookite was coupled with reduced graphene oxide (rGO). Most of TiO_2 -rGO composites reported are anatase, rutile or anatase/rutile TiO_2 with rGO and there is no report on brookite or two-phase anatase/brookite with rGO. In this study, we coupled

rGO with the as-synthesized two phase anatase/brookite TiO_2 via chemical reduction method to investigate the charge separation as well as the effect on hydrogen yield. Similarly, photoluminescence spectroscopy was used to provide evidence of the reduced probability of electron-hole pair recombination caused by the charge transfer from brookite and anatase TiO_2 to rGO.

For visible light harvesting, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) was used as it has band gap energy of 2.7 eV which is able to absorb light up to 450 nm. To further improve the visible light absorption of $\text{g-C}_3\text{N}_4$, we modified the band structure of $\text{g-C}_3\text{N}_4$ by introducing hydrogen gas during the heat treatment process of dicyandiamide. Various characterization methods and density functional theory based electronic structure calculations were employed to explain for the red-shifting of absorption of the $\text{g-C}_3\text{N}_4$ heated in hydrogen. To further enhance the hydrogen production and counter the fast electron-hole recombination, the hydrogen treated $\text{g-C}_3\text{N}_4$ was coupled with the two phase anatase/brookite TiO_2 .

The objectives of this study are to:

(1) Two-phase anatase/brookite TiO_2

- To develop methods to control the phase, morphologies and to enhance the photocatalytic activities of the TiO_2 photocatalysts.

- To understand the formation mechanism of the different TiO_2 phases by various characterization techniques and the charge transfer involved between the as-synthesized TiO_2 photocatalysts.

(2) rGO-anatase/brookite TiO_2

- To enhance the hydrogen production via photocatalytic water splitting by further improving the charge separation to reduce electron-hole pair recombination.

(3) g- C_3N_4 -anatase/brookite TiO_2

- To understand the effects of introducing hydrogen in the g- C_3N_4 synthesis method on the chemical and electronic structure, morphology, optical properties and photocatalytic activities of g- C_3N_4 .
- To enhance the solar-to hydrogen conversion efficiency by shifting the g- $\text{C}_3\text{N}_4/\text{TiO}_2$ mixtures photo-response to the visible light region.

1.8 Organization of the Thesis

This thesis is divided into five chapters. In the first chapter, background on the demand of hydrogen fuel, fundamentals of solar hydrogen production via photocatalytic water splitting, challenges faced in photocatalytic water splitting and various approaches to enhance the solar hydrogen production were introduced. In the second chapter, a simple hydrothermal method with titanium sulfide and sodium hydroxide as the precursors was presented to control the phases of TiO_2 synthesized (anatase, brookite

and/or sodium titanate) via the variation of sodium hydroxide concentration. The photocatalytic activities of the as-synthesized two-phase anatase/brookite TiO_2 was shown to be higher in comparison of pure anatase and brookite TiO_2 . In the third chapter, coupling of two-phase anatase/brookite TiO_2 with rGO was shown to enhance the hydrogen production due to the enhancement in charge separation and the reduction in recombination of electron-hole pairs. In the fourth chapter, for visible light harvesting, a modified synthesis method of $\text{g-C}_3\text{N}_4$ with the introduction of hydrogen gas in the polymerization process was shown to improve the visible light absorption and the photocatalytic activity of $\text{g-C}_3\text{N}_4$. The effects of introducing hydrogen in the $\text{g-C}_3\text{N}_4$ synthesis method on the chemical and electronic structure, morphology, optical properties and photocatalytic activities of $\text{g-C}_3\text{N}_4$ were discussed. In addition, by coupling two-phase anatase/brookite TiO_2 with $\text{g-C}_3\text{N}_4$, the hydrogen production via photocatalytic water splitting under visible light illumination increased as compared to pristine $\text{g-C}_3\text{N}_4$ (H_2), $\text{g-C}_3\text{N}_4$ (H_2) with single phase anatase, brookite, anatase/rutile and anatase/brookite/rutile TiO_2 . Lastly, conclusions and future recommendations for this project were addressed in the fifth chapter.

Chapter 2: Synergistic Two-phase Anatase/Brookite TiO₂ Nanostructures for Enhanced Photocatalytic Hydrogen Production

2.1 Introduction

Since the discovery of hydrogen production through water splitting over TiO₂ photoanode under the irradiation of UV light by Fujishima and Honda in 1972¹³, extensive research has been focused on TiO₂ as photocatalyst in water splitting due to its high photocatalytic activity, good photochemical stability in aqueous solution, high abundance and cost effectiveness^{42, 86-89}. TiO₂ exists commonly in three phases; rutile (tetragonal, P4₂/mmn), anatase (tetragonal, I4₁/amd), and brookite (orthorhombic, Pbca). All of them are formed by distorted TiO₆ octahedra and their structures are built up by different connection of TiO₆ octahedra as shown in Figure 2.1. In rutile polymorph, two opposing edges of each TiO₆ octahedron are shared to form linear chains which are linked by corner-sharing of oxygen atoms. In anatase polymorph, four edges are shared per octahedron and there is no corner oxygen sharing. In brookite polymorph, the octahedra share three edges and it has structure similar to rutile as both phases are formed by straight polyhedron chains linked through three corners of the unit cell but the linking of polyhedron chains occurs through cis bridges in brookite⁹⁰⁻⁹².

Figure 2.1 Representation of three TiO_2 polymorphs: anatase, rutile, and brookite ⁹².

As a bulk material, rutile is the thermodynamically stable phase while anatase and brookite are metastable. However, anatase phase is generally favoured in solution phase preparation methods which is attributed to two main factors: surface energy and solution chemistry ⁹³. At nanoscale, surface energy plays an important role of the total energy as the energies of the three TiO_2 phases are sufficiently close that the transformation sequence among the three TiO_2 phases can be reversed by small differences in surface energy. As a result, the transformation sequence will depend on the particles size and pH of the solutions ⁹⁴. Zhang et al. reported that if the three TiO_2 phases have the same particles size, at diameters less than 11 nm, anatase is the most thermodynamically stable phase while between 11 to 35 nm, brookite is the most stable phase. On the other hand, rutile is the most stable phase when particles size exceeds 35 nm ⁹⁵⁻⁹⁷. However, in very acidic solutions, rutile is stabilized relative to anatase whereas in very alkaline solutions, anatase is stabilized relative to rutile and brookite ^{94, 98, 99}.

TiO₂ can be synthesized by various methods such as thermolysis¹⁰⁰, sol-gel¹⁰¹⁻¹⁰³, hydrothermal^{104, 105}, solvothermal^{106, 107} and electrochemical spark discharge spallation¹⁰⁸. Among the various synthesis techniques, hydrothermal synthesis is a simple, low cost and environment friendly method¹⁰⁹. By far anatase and rutile are the most common phases synthesized and widely studied for the application as photocatalyst due to the ease of their synthesis⁹⁴. On the other hand, brookite is rarely studied due to its difficulty in synthesizing as it is furthest away from equilibrium under ambient conditions⁸³. However, it was reported that brookite nanocrystals have higher photocatalytic activities as compared to rutile and anatase^{84, 85}. Thus, in recent years there have been many methods in synthesizing brookite and as well as brookite mixtures with different Ti precursors. For example, Kiyama et al. synthesized brookite nanocrystals by aerial oxidation of titanium(III) chloride (TiCl₃) solution in sodium acetate at 95 °C under flowing air¹¹⁰. Pottier et al. synthesized brookite/rutile mixture with brookite as the major phase by thermolysis of TiCl₄ in concentrated HCl solutions¹¹¹. Kominami et al. synthesized brookite rod- or columnar-shaped particles by thermal treatment of oxobis(2,4-pentanedionato-O,O')titanium in ethylene glycol and sodium laurate solution at 300 °C¹¹². Murakami et al. prepared brookite nanocrystal by heating titanate nanotubes in perchloric acidic solution at 200 °C for 50 h by hydrothermal method¹¹³ and Music et al. synthesized brookite/anatase mixture by hydrolysis of titanium(IV) isopropoxide (TIP) in the presence of nitric acid¹¹⁴. In most of the synthesis processes, TiCl₄, TiCl₃, or titanium alkoxides are used as the Ti precursors and in some cases, highly acidic medium is involved as well. However, TiCl₄ and titanium alkoxides are sensitive to moisture as they hydrolyze easily in water or even in moist air, hence special care is

required in handling these chemicals such as submerging it in ice-cooled water bath or handling it under inert gas. Thus, it is challenging to synthesize brookite with a simple one-step synthesis method in aqueous medium.

Moreover, in comparison with single phase TiO_2 , mixed-phase TiO_2 has proven to have higher photocatalytic activities due to the presence of heterojunction^{90, 115}. As photocatalytic activity is limited by the fast electron-hole pair recombination, by having two phases of TiO_2 , electron can be transferred from one phase with more negative conduction band potential to another phase with less negative conduction band potential. As a result, the electron-hole pair recombination is suppressed due to effective charge separation⁹⁰. A well known example is P25, which is a commercial TiO_2 powder with 75 % of anatase and 25 % of rutile. With illumination of UV light on P25, photoexcited electrons from the anatase phase will be transferred to the rutile phase due to lower conduction band energy of the rutile phase and thus inhibiting charge recombination¹¹⁶. With much of the research focusing on the photocatalytic activities of anatase/rutile mixture, less attention has been paid to anatase/brookite mixture or rutile/brookite mixture due to the difficulty in synthesizing brookite TiO_2 phase. Although there are reports on brookite mixtures showing higher photocatalytic activities than the single phase TiO_2 and anatase/rutile mixture, there are only a few reports on tailoring the brookite ratio in the TiO_2 mixtures with controlled synthesis method. For example, Ozawa et al. showed that anatase-brookite composites have higher photocatalytic activities than single phase anatase TiO_2 by synthesizing anatase-brookite composite nanocrystals from the stirring of amorphous TiO_2 in 0.1 M of HCl solution and heat treating the resulting particles in air from 200 °C to 600 °C¹¹⁷. Etacheri et al. showed that

carbon-doped anatase-brookite nanoparticles have higher photocatalytic activities than anatase-rutile mixture by synthesizing carbon-doped anatase-brookite nanoparticles from amorphous TiO_2 synthesized from titanium tetraisopropoxide and crystallizing it by microwave irradiation at $100\text{ }^\circ\text{C}$ ¹¹⁸. Although both Ozawa et al. and Etacheri et al. were able to synthesize anatase-brookite mixtures but they were not able to control the brookite ratio in the TiO_2 mixtures. Xu et al. reported synthesizing brookite nanoparticles and rutile nanorods TiO_2 mixtures via hydrothermal method with tunable brookite to rutile ratio with the use of TiCl_4 and triethylamine as the precursors ¹¹⁹. By tuning the volume ratio of triethylamine to water, it was possible to control the brookite to rutile ratio in the mixed-phase TiO_2 . Kandiel et al. reported tailoring anatase to brookite ratio in anatase nanoparticles and brookite nanarods TiO_2 mixtures by tuning the urea concentration with titanium bis(ammonium lactato) dihydroxide as the titanium precursor ⁹⁴. Hence, it remains as a challenge to synthesize brookite TiO_2 mixture with a simple one-step process with tunable phase composition.

In this study, a simple hydrothermal method was developed to synthesize two-phase anatase/brookite TiO_2 mixture using titanium sulfide in alkaline sodium hydroxide medium. The ratio of anatase to brookite phase can be easily tailored with variation of sodium hydroxide concentration. Using titanium sulfide as a titanium source precursor has several advantages as it is soluble in water and hence an alcohol based solution is not required. Moreover, it is stable at room temperature in air and thus easy to handle. For comparison of photocatalytic activity, pure anatase nanoparticles and pure brookite nanoplates were synthesized with the same method.

2.2 Experimental Section

2.2.1 Hydrothermal Synthesis

200 mg of titanium sulfide, TiS_2 , (Sigma Aldrich) was added into 3.43 mL of sodium hydroxide (NaOH) of varying concentrations (0.5 M to 2 M) in a 23 mL Teflon cup. The suspension was stirred for 5 minutes before being sealed in a stainless steel autoclave and heated up in a conventional oven at 200 °C for various durations. Subsequently, the autoclave was cooled in air and the resulting powders were collected via centrifugation, washed with deionized water and dried at 80 °C.

2.2.2 Preparation of Pt Loaded TiO_2

0.3 wt% of Pt was loaded on the as-synthesized TiO_2 photocatalysts via photodeposition: the as-synthesized TiO_2 was dispersed in deionized water by ultrasonic agitation and methanol was added to the slurry in volume ratio of 1:1 to water. The required amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) was added into the suspension followed by Ultra Violet-Visible (UV-Vis) irradiation with a 800 W Xe-Hg lamp (Newport, USA) for 2 hours. The Pt loaded TiO_2 powders were collected via centrifugation, washed with deionized water and dried at 80 °C.

2.2.3 Characterization

The X-ray diffraction (XRD) patterns were obtained on a Bruker-AXS X-ray diffractometer using Cu K α radiation ($\lambda=1.54178$ Å). The phase analysis by the Rietveld method was carried out using TOPAS 4.0 software (Bruker AXS). The morphologies of the samples were examined by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-2010 and JEM-2100F). The surface areas were evaluated by nitrogen adsorption measurements on a Micromeritics ASAP 2010 adsorption analyzer. The band gaps of the as-synthesized anatase and brookite were determined by diffuse reflectance spectroscopy (Shimadzu 2550 UV-Vis-NIR spectrometer) with BaSO₄ as the reference standard. Photoluminescence (PL) spectra were collected from a spectrofluorophotometer (Shimadzu RF 5301 spectrofluorophotometer) at room temperature with the excitation wavelength of 325 nm.

2.2.4 Flatband Potential Measurement

The flatband potentials were measured by impedance spectroscopy using Mott-Schottky plots. To prepare for the test sample, 15 mg of the as-synthesized TiO₂ powder was sonicated in 1 mL of ethanol to obtain a homogenous mixture. The TiO₂ suspension was drop-casted on a conductive fluorine-tin oxide (FTO) glass with adhesive tapes which act as spacers attached on the 4 sides of the substrate. The substrate was then heated at 80 °C for drying and the adhesive tape attached on the top side of the substrate was removed. Electrical contact was formed by applying silver paint on the top uncoated area of FTO and sticking copper tape on the silver paint. Three electrodes were used for

the impedance measurements which include the working electrode (TiO₂ film), counter electrode (Pt plate) and reference electrode (Ag/AgCl, saturated KCl). 0.1 M of NaOH solution was used as the electrolyte. The measurements were carried out by Gamry electrochemical impedance spectroscopy and the potential was systemically varied between +0.2 to -1.2 V with frequency of 10, 50 and 100 Hz.

2.2.5 Femtosecond Transient Absorption Spectroscopy

The as-synthesized TiO₂ powder was drop-casted on quartz substrate to form a thin layer of film and the TiO₂ thin film was excited with a 325 nm pump pulses of power intensity of 100 μ W and probed with 570 nm probe pulses. The laser system comprises of a 1 kHz Coherent Legend regenerative amplifier seeded by a 80 MHz Coherent Vitesse 800 oscillator. The regenerative amplifier is used to pump the optical parametric amplifiers (OPA) – a Coherent TOPAS for wavelength tuning. For the transient absorption measurements, pump pulses from the OPA were focused onto a 200 micrometer spot and overlapped with white-light continuum probe pulses generated with a thin sapphire plate. Pump-induced changes were monitored using a monochromator/PMT configuration coupled to a lock-in amplifier. The pump beam was chopped at 83 Hz and used as the reference frequency for the lock-in.

2.2.6 Evaluation of Photocatalytic Activity

The photocatalytic hydrogen production was performed in a Pyrex glass vessel with a top quartz window for vertical illumination in a closed-gas circulation system. In a typical run, 45 mg of catalyst was suspended in 100 mL of aqueous methanol solution (20 vol %) in the glass reactor with stirring. The reaction temperature was maintained at 25 °C with the help of external water circulation. The reactor was then sealed up and repeatedly vacuumed by a rotary pump and purged with argon gas to remove the residual air. Subsequently, the reactor was irradiated with an 800 W Xe-Hg lamp (Newport, USA) from the top with light intensity of 245 mW cm^{-2} . Infrared (IR) component in the radiation was removed by the circulating water filter. The amount of generated H_2 gas was quantitatively analyzed every 1 hour by a gas chromatograph (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas).

2.3 Results and Discussion

2.3.1 Phase Composition

2.3.1.1 Phase Composition of Nanostructures Synthesized with Different Concentrations of Sodium Hydroxide

Figure 2.2 shows the XRD patterns of the TiO_2 powders synthesized from TiS_2 with various concentrations of NaOH (0.5 M, 0.9 M, 1 M, 1.2 M, 1.3 M, 1.5 M and 2 M) at 200 °C for 24 hours. Anatase TiO_2 has a characteristic 2θ value at around 25.3° corresponding to the (101) planes while brookite TiO_2 also has a characteristic 2θ value at around 25.3° which corresponds to the (120) planes. Thus, due to the closeness of these 2θ values, there is an overlapping of the anatase (101) and brookite (120) peaks.

Hence, to differentiate brookite from anatase, the most distinguish peak is the characteristic 2θ value at around 30.8° corresponding to the (121) planes of brookite. With 0.5 M of NaOH, pure anatase TiO_2 was formed while with the increase of NaOH concentration to 0.9 M, 1 M and 1.1 M, both anatase and brookite phases were formed. With 1.2 M of NaOH, pure brookite phase with no anatase phase was formed and with further increase of NaOH concentration to 1.3 M, sodium titanate which has characteristic 2θ value at 9.2° corresponding to the (200) planes was formed together with brookite phase. With 1.5 M and 2 M of NaOH, pure sodium titanate was formed.

Figure 2.2 XRD patterns of the nanostructures synthesized with various NaOH concentrations at 200°C for 24 hours. Curve A: 0.5 M NaOH; curve B: 0.9 M NaOH; curve C: 1 M NaOH; curve D: 1.1 M NaOH; curve E: 1.2 M NaOH; curve F: 1.3 M

NaOH; curve G: 1.5 M NaOH; and curve H: 2 M NaOH. Symbol °, * and + denote anatase (Joint Committee on Powder Diffraction Standards (JCPDS) 21-1272), brookite (JCPDS 29-1360) and sodium titanate (JCPDS 47-0124) respectively.

To understand the mechanism of formation of the phases, Rietveld refinement was performed to determine the composition of anatase and brookite phases present in the mixture as shown in Figure 2.3. With increasing concentration of NaOH, the amount of brookite increases till at 1.2 M of NaOH where 100 wt% of brookite is formed. When TiS_2 is added into the NaOH solution, hydrolysis reaction occurs leading to the formation of $\text{Ti}(\text{OH})_x^{4-x}$ complex as follows:

Both Yin et al. and Testino et al. reported that under acidic condition in aqueous medium in which the number of OH ligands is limited, corner-shared bonding is favored over edge-shared bonding as edge-shared bonding requires two condensations between pairs of Ti^{4+} centers to occur simultaneously. As a result, corner-shared bonding is preferred which leads to the formation of rutile phase. However, at alkaline conditions, with higher concentration of OH ligands, the number of OH coordinated to Ti^{4+} centers increases and hence favoring the formation of edge-shared bonding which leads to the formation of anatase phase as shown in Figure 2.4^{120, 121}. Thus, at 0.5 M of NaOH, pure anatase was formed instead of rutile.

Figure 2.3 Composition of anatase and brookite determined from Rietveld refinement analysis synthesized with various NaOH concentrations at 200 °C for 24 hours.

Figure 2.4 Formation of anatase and rutile based on partial charge model ¹²⁰.

However, with higher concentration of NaOH, brookite phase started to form and as the concentration of NaOH increases, the amount of brookite phase increases. This is similar to the results that Kandiel et al. found where he used titanium bis(ammonium lactate) dihydroxide (TALH) and urea as the precursors⁹⁴. At low OH⁻ concentrations, the OH⁻ ions is only sufficient for slow hydrolysis of the Ti precursor leading to formation of pure anatase phase. As the concentration of OH⁻ ions increases, it leads to rapid thermal hydrolysis of the Ti precursor and hence resulting in the formation of both anatase and brookite seeds. As a result, with increase of NaOH concentration, it favors the formation of brookite phase.

2.3.1.2 Phase Composition of Nanostructures Synthesized with Different Growth Time

To understand the mechanism of the formation of the two-phase anatase/brookite TiO₂, the effect of growth time on the phase composition of anatase and brookite mixture was studied with fixed NaOH concentration of 1 M. Figure 2.5 presents the XRD patterns of the nanostructures synthesized with 1 M of NaOH at 200 °C for various growth time from 1 to 24 hours. At short growth time of 1 hour, pure sodium titanate was formed and with growth time of 3 hours, a mixture of three phases of sodium titanate, anatase and brookite were formed. With increasing growth time, mixtures of anatase and brookite without sodium titanate were obtained from 6 to 24 hours. Thus, this observation is suggestive that anatase and brookite phases were formed by the transformation of sodium titanate. Deng et al. demonstrated that brookite phase can be formed from sodium titanate by releasing Na⁺ from the surface accompanied by oxidation of Ti in the structure as

shown in Figure 2.6¹²². To prove that the anatase and brookite were formed by the transformation of sodium titanate, Rietveld refinement was performed to determine the composition of anatase and brookite phases present in the mixture.

Figure 2.5 XRD patterns of the nanostructures synthesized with 1 M of NaOH at 200 °C for various reaction times. Curve A: 1 h; curve B: 3 h; curve C: 6 h; curve D: 10 h; curve E: 14 h; curve F: 18 h; and curve G: 24 h. Symbol °, * and + denote anatase, brookite and sodium titanate respectively.

Figure 2.6 A possible model for the transformation of titanate to brookite by releasing Na^+ or H^+ accompanied by oxidation of Ti in the structure¹²².

Figure 2.7 shows the composition of anatase and brookite in the powders synthesized with 1 M of NaOH concentration at 200 °C for various growth times. From the Rietveld analysis, the ratio between anatase and brookite remains almost similar from 6 to 24 hours. The small difference in the compositions of anatase and brookite between 6 to 24 hours could be attributed to the experimental variation. Thus, growth times greater than 6 hours have no effect on the ratio between anatase and brookite. Hence, this further proves the speculation that anatase and brookite were formed by the transformation of sodium titanate as all sodium titanate nanostructures had been transformed into anatase and brookite resulting in no further changes in the composition of anatase and brookite with

growth time of 6 hours or longer. To further prove that the formation of anatase and brookite is not caused by the transformation of amorphous content, the amount of amorphous content is determined by spiking the as-synthesized powders with 50 wt% of CaF_2 as reference material. From Rietveld refinement, there is almost negligible amount of amorphous content present for the anatase/brookite TiO_2 with growth time of 6 hours and more due to the good crystallinity obtained from a high hydrothermal temperature of 200 °C. As a result, this further proves our speculation that the anatase and brookite were formed by the transformation of sodium titanate. Figure 2.8 shows the schematic formation of layered titanate from the hydrolysis of TiS_2 and the ololation of the TiO_6 octahedra which in turn transform into anatase and brookite phases.

Figure 2.7 Composition of anatase and brookite determined from Rietveld refinement analysis synthesized with 1 M of NaOH at 200 °C for various reaction times.

Figure 2.8 Schematic of formation of sodium titanate from titanium sulfide into anatase and/or brookite ²¹.

To further prove our speculation that the anatase and brookite were formed by the transformation of sodium titanate, the powders were synthesized with various reaction times with fixed concentration of NaOH of 0.5 M and 1.2 M and the XRD patterns of these powders are shown in Figure 2.9 and 2.10 respectively. As shown in Figure 2.9, with 0.5 M of NaOH, only sodium titanate was formed at short reaction time of 10 minutes. As growth time increases to 1 hour, anatase started to form together with sodium titanate. With growth time of 3 h onwards, only anatase was formed. Thus, this observation further proves that sodium titanate was first formed followed by the transformation of sodium titanate to anatase and subsequently the complete transformation of sodium titanate to anatase. At higher NaOH concentration of 1.2 M, similarly, at short reaction time of 1 hour, sodium titanate was first formed, followed by

sodium titanate and brookite mixture and subsequently pure brookite was formed as reaction time increases as shown in Figure 2.10. Figure 2.11 shows a summary of TiO_2 phases formed with various concentrations of NaOH and reaction times. In summary, the concentration of NaOH plays an important role in controlling the phases and anatase/brookite ratio.

Figure 2.9 XRD patterns of the nanostructures synthesized with 0.5 M of NaOH at 200 °C for various reaction times. Curve A: 10 minutes; curve B: 0.5 h; curve C: 3 h and curve D: 24 h. Symbol °, * and + denote anatase, brookite and sodium titanate respectively.

Figure 2.10 XRD patterns of the nanostructures synthesized with 1.2 M of NaOH at 200 °C for various reaction times. Curve A: 1 h; curve B: 3h; curve C: 6 h; curve D: 8 h; curve E: 14 h; curve F: 20 h; curve G: 22 h; and curve H: 24 h. Symbol * and + denote brookite and sodium titanate respectively.

Figure 2.11 Summary of TiO_2 phases formed with various reaction times and various NaOH concentrations: a) 0.5 M of NaOH, b) 1.0 M of NaOH and c) 1.2 M of NaOH. A, B and T denote anatase, brookite and sodium titanate respectively.

2.3.2 Morphologies

2.3.2.1 Morphologies of Nanostructures Synthesized with Different Concentrations of Sodium Hydroxide

Figure 2.12 and 2.13 show the morphologies of the nanostructures synthesized with various NaOH concentrations at 200 °C for 24 hours. From the FESEM image of Figure 2.12a, anatase nanoparticles of less 100 nm which are non-uniformly distributed were obtained with 0.5 M of NaOH. From the TEM images of Figure 2.13a and 2.13b, the size of anatase nanoparticles ranges from 18 to 42 nm. With 1.2 M of NaOH, the brookite phase which is in the shape of nanoplate was obtained and is non-uniformly distributed as

observed in the FESEM image of Figure 2.12e. From the TEM images of Figure 2.13c and 2.13d, the size of brookite nanoplates is bigger and is in the range of 120 to 400 nm.

From Figure 2.12b, 2.12c and 2.12d, with increasing concentration of NaOH (0.9 to 1.1 M of NaOH), mixture of nanoparticles predominantly with some nanoplates was obtained. From the previous results that anatase and brookite are in the shape of nanoparticles and nanoplates respectively, we propose that the mixture consists of anatase nanoparticles predominantly with some brookite nanoplates which is in agreement with the Rietveld refinement analysis reported earlier in Figure 2.3 that anatase is the main phase in the mixture with higher composition percentage.

From Figure 2.12f, with higher concentration of 1.3 M of NaOH, nanorods with nanoplates were formed and with further increase of NaOH concentration to 1.5 M and 2 M, sodium titanate nanowires were obtained as shown in Figure 2.12g and 2.12h.

Figure 2.12 FESEM images of nanostructures synthesized with various NaOH concentrations at 200 °C for 24 hours: a) 0.5 M of NaOH, b) 0.9 M of NaOH, c) 1 M of

NaOH, d) 1.1 M of NaOH, e) 1.2 M of NaOH, f) 1.3 M of NaOH, g) 1.5 M of NaOH and h) 2 M of NaOH.

Figure 2.13 a, b) TEM and HRTEM images of anatase nanoparticles synthesized with 0.5 M of NaOH at 200 °C for 24 hours and c, d) brookite nanoplates synthesized with 1.2 M of NaOH at 200 °C for 24 hours.

2.3.2.2 Morphologies of Nanostructures Synthesized with Different Growth Time

Figure 2.14 shows the morphologies of the nanostructures synthesized with 1 M of NaOH at 200 °C for various growth times from 1 to 24 hours. From Figure 2.14a, with short reaction time of 1 hour, pure sodium titanate nanorods were formed and with 3 hours of growth time, mixture of nanoparticles with small amount of nanoplates and nanorods was obtained as shown in Figure 2.14b. As evidenced by the XRD patterns (Figure 2.5) discussed earlier in Chapter 2.3.1.2, these three nanostructures are anatase, brookite and sodium titanate. From Figure 2.14c to 2.14g, with growth time of 6 to 24 hours, mixture of anatase nanoparticles and brookite nanoplates was formed. From the TEM image of Figure 2.15a, at growth time of 10 hours, the anatase nanoparticle is approximately 24 nm while the brookite nanoplate is approximately 53 nm. At growth time of 24 hours (Figure 2.15b), the anatase nanoparticle is approximately 24 nm while the brookite nanoplate is approximately 56 nm.

Figure 2.14 FESEM images of the nanostructures synthesized with 1 M of NaOH at 200 °C for various growth times: a) 1 h, b) 3 h, c) 6 h, d) 10 h, e) 14 h, f) 18 h and g) 24h.

Figure 2.15 TEM images of nanostructures synthesized with 1 M of NaOH at 200 °C for a) 10 h and b) 24h.

2.3.3 BET Surface Area

Table 2.1 shows the BET surface area analyzed by nitrogen adsorption for the nanostructures synthesized with 1 M of NaOH at 200 °C for reaction time between 1 to 24 hours and with 0.5 M and 1.2 M of NaOH at 200 °C for 24 hours. At reaction time of 1 hour with 1 M of NaOH, the surface area of the nanostructure is the highest which could be due to the nanowires morphology and titanate layered crystal structure with large interplanar distance. At reaction time of 3 hours, due to the presence of sodium titanate phase which has higher surface area in the three phases mixture, the surface area is higher than the two-phase anatase/brookite mixture synthesized with longer reaction time of 6 hours or more. As the reaction time increases from 6 to 24 hours, there is a gradual decrease in surface area. This gradual decrease in surface area is due to the

increase in particle size which results in lower surface area to volume ratio. With 0.5 M of NaOH, the pure anatase nanoparticles have surface area of $44.61 \text{ m}^2 \text{ g}^{-1}$ while with 1.2 M of NaOH, pure brookite nanoplates have smaller surface area of $30.54 \text{ m}^2 \text{ g}^{-1}$ as these brookite nanoplates are bigger in size as evidenced by FESEM images in Figure 2.12a and 2.12e. From the isotherm nitrogen adsorption graph in Figure 2.16, the as-synthesized nanostructures are mesoporous with pore sizes of approximately 2 to 40 nm as shown in the inset of Figure 2.16.

Table 2.1 BET surface areas and pore volumes of sodium titanate (ST), anatase (A) and brookite (B) nanostructures synthesized with various concentrations of NaOH at 200 °C for various reaction times.

Synthesis Conditions	Polymorphs	BET Surface Area ($\text{m}^2 \text{ g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{ g}^{-1}$)
1 M NaOH-1 h	ST, A and B	81.05	0.18
1 M NaOH-3 h	ST, A and B	53.40	0.16
1 M NaOH-6 h	A and B	28.86	0.12
1 M NaOH-10 h	A and B	25.36	0.11
1 M NaOH-14 h	A and B	23.77	0.09
1 M NaOH-18 h	A and B	24.41	0.10
1 M NaOH-24 h	A and B	19.36	0.10
0.5 M NaOH-24 h	A	44.61	0.29
1.2 M NaOH-24 h	B	30.54	0.09

Figure 2.16 Isotherm N₂ sorption of sodium titanate, anatase and brookite nanostructures synthesized with various concentrations of NaOH at 200 °C for various growth times. 1 M of NaOH with various reaction times: a) 1 h, b) 3 h, c) 6 h, d) 10 h, e) 14 h, f) 18 h and g) 24h. h) 0.5 M of NaOH for 24 h and i) 1.2 M of NaOH for 24h. Inset shows the pore volume distribution.

2.3.4 Flatband Potentials of Anatase and Brookite TiO₂

As discussed earlier in the introductory Chapter 1.5, the band edge potentials of the semiconductor photocatalyst play an important role in photocatalytic water splitting as the electrochemical potential of the holes in the valence band of the semiconductor has to be more positive than the redox potential of O₂/H₂O (+1.23 V vs. NHE at pH 0) in order

to oxidize water to oxygen and for hydrogen production, the electrons in the conduction band of semiconductor need to have potential more negative than the redox potential of H^+/H_2 (0 V vs. NHE at pH 0). There are various methods to determine the flatband potential of the semiconductor which include measuring the photopotential as a function of radiation intensity, the onset of the photocurrent or the capacitance of the space charge region¹²³. In this study, measuring the apparent capacitance as a function of potential under depletion condition is employed to determine the flat band potential of anatase and brookite TiO_2 . This method is based on the Mott-Schottky relationship as shown on equation 3.1:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon\epsilon_0 N} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (\text{equation 3.1})$$

where C_{sc} = capacitance of the space charge region, e = electron charge (1.602×10^{-19} C), ϵ = dielectric constant of the semiconductor, ϵ_0 = permittivity of free space (8.85×10^{-14} F cm^{-1}), N = donor density (electron donor concentration for n-type semiconductor or hole acceptor concentration for p-type semiconductor), E = applied potential, E_{fb} = flatband potential, k = Boltzmann constant (1.38×10^{-23} J K^{-1}) and T is the absolute temperature.

Thus, by plotting $\frac{1}{C^2}$ versus E and extrapolating the graph to the potential axis where $\frac{1}{C^2} = 0$, the flatband potential can be determined. Figure 2.17a and 2.17b show the Mott-Schottky plots for anatase nanoparticles and brookite nanoplates respectively and the flatband potentials of anatase nanoparticles and brookite nanoplates are found to be -1.01

V and -1.10 V vs. Ag/AgCl respectively. To convert the potential to be against the normal hydrogen electrode (NHE), 0.197 V has to be added according to equation 3.2:

$$E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V} \quad (\text{equation 3.2})$$

The flatband potentials of anatase nanoparticles and brookite nanoplates are -0.813 V vs. NHE and -0.903 V vs. NHE respectively at pH 12.57 as measurement was done in 0.1 M of NaOH. In order to compare it with other potential values in the literature, it is desirable to convert it to be at pH 0 or pH 7 with equation 3.3:

$$E_F(\text{pH}) = E_F + 0.059 (\text{pH}_0 - \text{pH}) \quad (\text{equation 3.3})$$

Hence, the flatband potentials of anatase nanoparticles and brookite nanoplates are -0.07 V and -0.16 V vs NHE at pH 0 (or -0.48 V and -0.57 V vs NHE at pH 7) respectively. Kandiel et al. reported that the flatband potentials of anatase nanoparticles and brookite nanorods are -0.35 V and -0.54 V vs NHE at pH 7 respectively ²¹. The difference of the measured flatband potential values with the reported values is small and could be due to the difference in particles size as size quantization could change the band gap resulting in different conduction band potential. In sum, the conduction band potential of anatase is just slightly more negative than the redox potential of H^+/H_2 (0 V vs. NHE at pH 0) while the conduction band potential of brookite is cathodically higher than the conduction band of anatase. With a higher cathodic conduction band potential, in theory it energetically favors proton reduction to form hydrogen gas resulting in a higher rate in photocatalytic hydrogen production. Our results on the photocatalytic hydrogen production will be presented and discussed in the next section.

Figure 2.17 Mott-Schottky plots obtained at different frequencies for TiO_2 film electrodes prepared with a) anatase nanoparticles synthesized with 0.5 M of NaOH at 200 °C for 24 h and b) brookite nanoplates synthesized with 1.2 M of NaOH at 200 °C for 24 h

h. Ag/AgCl, saturated KCl reference electrode and Pt counter electrode were immersed in 0.1 M NaOH electrolyte with pH 12.57.

2.3.5 Hydrogen Production via Photocatalytic Water Splitting with As-Synthesized TiO₂ Nanostructures

The amount of hydrogen gas evolved per gram of catalyst per hour in aqueous methanol solution over 0.3 wt% Pt loaded photocatalyst under UV-Vis light illumination is presented in Figure 2.18. From Figure 2.18a, pure sodium titanate synthesized with 1 M of NaOH for 1 hour generates the lowest amount of H₂ which could be due to the poor crystallinity of sodium titanate as evidenced by the broad XRD peak in Figure 2.5. With poorer crystallinity, there could be localized defect sites which are at potential lower than the conduction band and thus photogenerated electrons can be trapped there and not able to reduce protons to form H₂. As a result, lower amount of H₂ was generated. Comparing the single phase TiO₂, pure anatase nanoparticles generate lower amount of H₂ as compared to pure brookite nanoplates despite anatase nanoparticles having higher surface area as shown in Table 2.1. This is due to the more cathodic potential of brookite conduction band and the longer electron lifetime (the electron lifetime measurement will be shown in the next section via the transient absorption spectroscopy spectra) as compared to anatase which favors water reduction to produce more H₂.

To highlight the advantage of the as-grown two-phase photocatalysts, pure anatase and brookite nanostructures synthesized with 0.5 M of NaOH and 1.2 M of NaOH at 200 °C for 24 hours were physically mixed by using mortar and pestle into mixture of 88 % of

anatase and 12 % of brookite to have about the same composition as the as-synthesized two-phase anatase/brookite TiO_2 . Compared to single-phase TiO_2 , the as-synthesized two-phase anatase/brookite TiO_2 , physically mixed anatase and brookite TiO_2 and P25 all have higher H_2 evolution than pure anatase and brookite. P25 is a widely used commercial TiO_2 powder with 75 % of anatase and 25 % of rutile and surface area of $50 \text{ m}^2 \text{ g}^{-1}$ with high photocatalytic activity. The high photocatalytic activity of mixed-phase P25 is attributed to the transfer of electrons from anatase conduction band to the lower-energy rutile conduction band which leads to effective electron-hole separation and higher photocatalytic activity¹¹⁵. Similarly, electrons transfer from the brookite conduction band to the anatase conduction band in as-synthesized and physically mixed anatase/brookite TiO_2 have also demonstrated effective electron-hole separation and hence resulting in higher H_2 evolution (Figure 2.19).

In addition, the as-synthesized two-phase anatase/brookite TiO_2 and physically mixed anatase/brookite TiO_2 perform better than P25 with higher H_2 evolution despite P25 having higher surface area. By normalizing the hydrogen yield with respect to unit surface area, the as-synthesized two-phase anatase/brookite TiO_2 is 150 % more active than physically mixed anatase/brookite TiO_2 and 220 % more active than P25 (Figure 2.18b). The higher activity for anatase/brookite over P25 is attributed to the higher cathodic potential of brookite conduction band which energetically favors the reduction of protons to produce H_2 . In P25, the photo-reduction occurs either in the conduction band of anatase or rutile (after the charge injection), the reduction power of the bands is respectively lower than the one of brookite and anatase mixture, as rutile has less cathodic conduction band potential (0.07 V vs. NHE at pH 0) than the redox potential of

H^+/H_2 (0 V vs. NHE at pH 0)^{124, 125}. As a result, higher activity of our brookite/anatase mixture is achieved as compared to anatase/rutile mixture. Meanwhile, the physically mixed anatase and brookite mixture shows lower H_2 evolution as compared to the as-synthesized two-phase anatase/brookite TiO_2 . This proves the importance of interfacial contact in a two-phase photocatalyst. The relatively low activity of the physically mixed phase is clearly due to the poor interfacial contact between anatase and brookite phases resulting in less effective transfer of electrons from brookite to anatase and thus leading to less effective electron-hole separation. Therefore, the as-synthesized two-phase anatase/brookite TiO_2 produces the highest H_2 evolution due to both the more cathodic potential of brookite conduction band and more effective charge transfer leading to reduction in electron-hole recombination (which will be shown in the next section by the electron lifetime from femtosecond transient absorption spectroscopy).

The hydrogen evolution with nanostructures synthesized with 1 M of NaOH from 1 to 24 hours is shown in Figure 2.18c. Among the nanostructures synthesized with 1 M of NaOH at 200 °C for various reaction times from 1 to 24 hours, pure sodium titanate synthesized for 1 h and three-phase sodium titanate, anatase and brookite TiO_2 synthesized for 3 hour have lower H_2 evolution as compared to the nanostructures synthesized with other reaction times. This is due to the presence of sodium titanate with poor crystallinity and localized defect sites which result in lower H_2 evolution. Two-phase anatase/brookite TiO_2 synthesized with growth time of 14 hours produces the highest H_2 evolution ($3.77 \text{ mmole g}^{-1} \text{ h}^{-1}$). This could be due to the optimal combination of surface area and crystallinity where as growth time increases, the crystallinity will be improved while the surface area will decrease.

Figure 2.18 a) Hydrogen evolved per gram of catalyst per hour under UV-Vis irradiation in aqueous methanol solution over 0.3 wt% Pt loaded photocatalysts; sodium titanate nanowires synthesized with 1 M of NaOH at 200 °C for 1 h, two-phase anatase/brookite TiO₂ synthesized with 1 M of NaOH at 200 °C for 24 h, pure anatase nanoparticles synthesized with 0.5 M of NaOH at 200 °C for 24 h, pure brookite nanoplates synthesized with 1.2 M of NaOH at 200 °C for 24 h, commercial P25 and physically mixed anatase (88 wt%) and brookite mixture (12 wt%). b) Normalized hydrogen evolution (μmole g⁻¹ h⁻¹) per unit surface area with as-synthesized two-phase anatase/brookite TiO₂, commercial P25 and physically mixed anatase (88 wt%) and brookite mixture (12 wt%). c) Hydrogen evolved per gram of catalyst per hour with nanostructures synthesized with 1 M of NaOH at 200 °C for various growth time from 1 to 24 h.

Figure 2.19 Schematic of transfer of photogenerated electron from the conduction band of brookite to the conduction band of anatase under UV-Vis irradiation. Positions of as-synthesized anatase and brookite TiO₂ band edges relative to redox potential of water vs NHE at pH 0 are determined from Mott-Schottky analysis.

With brookite having a more cathodic conduction band, during the photodeposition process of 0.3 wt% of Pt loading on two-phase anatase/brookite TiO₂, more Pt co-catalyst could be photo-reduced and loaded on brookite phase than anatase phase. With more Pt co-catalyst, more photogenerated electrons at brookite conduction band could be transferred to Pt co-catalyst resulting in effective charge separation and further enhancement of H₂. To prove that the enhancement of H₂ production of the two-phase anatase/brookite system is mainly attributed to the more cathodic conduction band of the brookite phase which favor water reduction to form H₂ and not due to more Pt loading at

the brookite phase, pure anatase and pure brookite were loaded with 0.3 wt% of Pt separately and then physically mixed together. Figure 2.20 graph (a) shows the H_2 evolution with 0.3 wt% of Pt on anatase and 0.3 wt% Pt on brookite where Pt was first loaded on anatase and brookite separately and subsequently physically mixed with composition of 88 wt% of anatase and 12 wt% of brookite. When anatase and brookite were separately loaded with 0.3 wt% of Pt, the amount of Pt loaded on anatase and brookite should be the same which is 0.3 wt%. Figure 2.20 graph (b) shows the H_2 evolution with physically mixed anatase and brookite with composition of 88 wt% of anatase and 12 wt% of brookite which were then loaded with 0.3 wt% of Pt. From the H_2 evolution results, when anatase and brookite were separately loaded with 0.3 wt% of Pt and then physically mixed, it produces about the same amount of H_2 as compared to when anatase and brookite were physically mixed first and then loaded with 0.3 wt% of Pt. This shows that the enhancement of H_2 production of the two-phase anatase/brookite system is mainly attributed to the more cathodic conduction band of the brookite phase and the H_2 production is not mainly affected by the different amount of Pt loaded on brookite as compared to anatase but on the overall amount of Pt loaded on anatase and brookite where different amount of Pt loading will result in different amount of H_2 being produced^{89, 126-128}. Although Pt loading can enhance the H_2 production due to effective charge separation but there is an optimal amount of Pt to be loaded whereby after this amount of Pt loading, the H_2 production will decrease. This is because with too much of Pt particles on the surface of the photocatalyst, it can block the photosensitive TiO_2 surface and scatter the UV light to decrease the absorption by TiO_2 ¹²⁶. In addition, Pt particles may occupy the active sites on the surface of TiO_2 leading to the decrease of

surface active sites on TiO_2 and the concentration of the released protons⁴³. Pt particles may also act as the recombination centers for photogenerated electrons and holes and thus leading to the decrease of H_2 production^{43, 126}. Generally, maximum H_2 yield is observed with Pt loading of 0.3 to 1 wt%⁴³.

Figure 2.20 Hydrogen evolved per gram of catalyst with (a) physically mixed anatase with 0.3 wt% of Pt and brookite with 0.3 wt% of Pt in composition of 88 wt% of anatase and 12 wt% of brookite and (b) 0.3wt% of Pt on physically mixed 88 wt% of anatase and 12 wt% of brookite. A and B denote anatase and brookite.

The stability of two-phase anatase/brookite TiO_2 was investigated for running 3 cycles of photoreaction over a total of 18 hours with 0.3 wt% Pt loaded two-phase

anatase/brookite TiO_2 photocatalyst synthesized with 1 M of NaOH at 200 °C for 14 h. After each cycle of 6 hours, the system was repeatedly vacuumed by a rotary pump and purged with argon gas to remove the H_2 produced. The amount of H_2 evolved decreases after the first run and remains almost the same in the second and third run suggesting the two-phase anatase/brookite TiO_2 is photo-chemically stable over a long period of time.

Figure 2.21 Stability test for 0.3 wt% Pt loaded two-phase anatase/brookite TiO_2 photocatalyst synthesized with 1 M of NaOH at 200 °C for 14 h in 3 continuous runs with evacuation at every 6 hours.

Overall, our as-synthesized two-phase anatase/brookite TiO_2 has the highest H_2 evolution as compared to pure anatase, brookite and the widely used P25 photocatalyst where the as-synthesized two-phase anatase/brookite TiO_2 (1 M NaOH for 14 h) produces 1.29 times of H_2 produced from P25. This is mainly due to more cathodic

conduction potential of brookite phase than anatase phase and the effective charge separation due to the charge transfer from brookite to anatase conduction band.

2.3.6 Lifetime of Excited Electrons in As-Synthesized TiO₂ Nanostructures

To determine the dynamics of the excited electrons in the TiO₂ nanostructures, femtosecond transient absorption (TA) spectroscopy was employed with 325 nm pump excitation. The probe wavelength chosen was 570 nm, where the TA signals were dominated by the absorption of trapped holes and a small contribution from the trapped electrons^{129, 130}. Figure 2.22 shows the temporal profiles of the as-synthesized pure anatase, brookite and two-phase anatase/brookite TiO₂ mixture. These decay profiles were well fitted with biexponential decay kinetics which has been shown to describe electron-hole recombination in quantum sized TiO₂¹³¹. The fitted lifetimes are summarized in the inset table of Figure 2.22, where τ_1 represents the initial decay arising from the recombination of the surface-trapped electrons/hole and τ_2 represents the longer decay involving the recombination of the interstitially trapped electrons with the holes¹³². From the TA spectroscopy results, photogenerated electrons in pure brookite phase have longer lifetimes (τ_2) compared to pure anatase phase. Similarly, Yamada et al. reported that photogenerated electrons have longer lifetimes in anatase phase compared to rutile phase and pointed out that the longer electron lifetime is related to the high photoactivity of anatase¹³³. Given the higher cathodic conduction band potential and longer photogenerated electron lifetime, it is understandable that H₂ evolution is higher for the brookite phase compared to the anatase phase - as validated in Chapter 2.3.5.

On the other hand, the as-synthesized anatase/brookite TiO_2 exhibit similar lifetimes as the pure anatase phase, which are shorter than the pure brookite phase (but are still in the same nanosecond timescale). Lifetime alone may not be a clear indication of the photoactivity. Correlating with the data from the H_2 evolution studies, these shorter lifetimes observed in the two-phase anatase/brookite TiO_2 could be interpreted as a consequence of fast electron transfer from the brookite conduction band to the anatase conduction band and the shorter path taken for electrons to recombine with hole due to lower band gap energy of anatase than brookite phase. This is also understandable given the higher percentage of the anatase phase over the brookite phase in the two-phase anatase/brookite TiO_2 . Furthermore, many researchers have shown that in samples with good interfacial contact, electrons can be transferred from the conduction band of one phase to the conduction band of another phase with lower conduction band potential^{116, 134-137}. A well known example is the electron transfer from the more cathodic anatase conduction band to the rutile conduction band. Kawahara et al. evidenced that the excited electrons are transferred from anatase conduction band to rutile conduction band in patterned anatase–rutile bilayer-type photocatalyst which leads to higher photoactivity than pure anatase or rutile photocatalyst¹³⁴. Moreover, with strong coupling and good interfacial contact, the electron transfer can be ultra-fast and even faster than electron-hole recombination. Masumoto et al. showed that the electron transfer from PbSe quantum dots to the porous TiO_2 film takes place in picosecond range which is much faster than the electron-hole recombination lifetime¹³⁵. Manga et al. reported in hybrid graphene–titania materials, ultrafast electron transfer occurs within 200 fs¹³⁶ and Long et

al. reported energy relaxation in graphene takes place in a few hundred femtoseconds and electron transfer from graphene to TiO₂ is 3 to 5 times faster than energy relaxation¹³⁷.

Figure 2.22 Transient absorption spectroscopy profiles following a 325 nm laser pulse excitation of the pure anatase, pure brookite and two-phase anatase/brookite TiO₂ films where the differential absorbance is plotted as a function of delay time. The inset table shows the fitted lifetimes and pre-exponential factors.

Similarly, photoluminescence (PL) emission spectroscopy is a common technique used to study the transfer, separation and recombination behavior of the photogenerated electrons and holes in semiconductor materials¹³⁸. When the photogenerated electrons

and holes recombine, photons are emitted resulting in photoluminescence. Generally, with lower PL intensity, it suggests lower recombination rate of photogenerated electron-hole pairs. Figure 2.23 shows the PL spectra for pure anatase, brookite and two-phase anatase/brookite TiO_2 with emission peak at 378 nm which is approximately equal to the band gap of TiO_2 (388 nm for anatase and 376 nm for brookite) ¹³⁹ and thus this peak corresponds to the direct electron-hole recombination. The emission band from 400 to 500 nm arises from indirect band gap and surface recombination processes ¹⁴⁰. From Figure 2.23, the PL intensity of the 378 nm peak is the lowest with two-phase anatase/brookite TiO_2 , followed by brookite phase and lastly anatase phase. This shows that with two phases in the sample, the probability of electron-hole recombination is lower and hence enhances the photocatalytic activity. The PL intensity is lower with brookite as compared to anatase phase which is similar to the TA spectroscopy results where photogenerated electrons in pure brookite phase have longer lifetimes compared to pure anatase phase. Both indicate that brookite has lower probability of electron-hole recombination than anatase phase and thus leading to enhancement of H_2 due to synergistic effect of more cathodic potential of brookite conduction band and the longer electron lifetime.

Figure 2.23 Photoluminescence spectra of anatase, brookite and two-phase anatase.brookite TiO_2 .

2.4 Conclusions for the Chapter

In conclusion, highly crystalline brookite nanoplates and two-phase anatase/brookite TiO_2 were successfully synthesized via a simple hydrothermal method with TiS_2 in NaOH solution. With variation of the NaOH concentration and reaction time, the phase composition of two-phase anatase/brookite TiO_2 mixture is controllable. Further investigation on phase transformation conducted by time-evolved hydrothermal reaction indicates that anatase and brookite are formed from the direct transformation of sodium titanate. Photocatalytic activities of the as-synthesized two-phase anatase/brookite TiO_2

were evaluated by hydrogen evolution via water splitting. Despite anatase nanoparticles having higher surface area than brookite nanoplates, higher H_2 evolution was obtained with brookite nanoplates. This is attributed to the more cathodic potential of the brookite conduction band and the long excited electrons lifetime which favor the reduction of water to produce H_2 . Moreover, higher H_2 evolution was obtained with the as-synthesized two-phase anatase/brookite TiO_2 as compared to pure brookite nanoplates. This is likely due to the electrons transfer from brookite conduction band to anatase conduction band and thus resulting in effective electron-hole separation. In addition, the as-synthesized two-phase anatase/brookite TiO_2 generates even higher amount of H_2 as compared to the widely used commercial P25.

To further enhance the charge separation and the hydrogen production, the as-synthesized anatase/brookite was coupled with reduced graphene oxide (rGO) which will be discussed in Chapter 3.

Chapter 3: Further Enhancement of Photocatalytic H₂ Production with Reduced Graphene Oxide-Anatase/Brookite TiO₂ Mixtures

3.1 Introduction

To further improve the photocatalytic activity of TiO₂, one of the strategies includes inhibiting the electron-hole recombination. It involves coupling TiO₂ with another material with less cathodic conduction band potential and/or less anodic valence band potential than TiO₂. Various studies have shown that TiO₂ with carbon composites including carbon nanotubes (CNTs) and fullerenes enhance the photocatalytic performance as compared to TiO₂ alone¹⁴¹⁻¹⁴⁵ due to effective charge separation. However, there are several drawbacks with TiO₂-CNT and TiO₂-fullerene composites such as weakening of light intensity arriving at the surface of the catalyst, insolubility of CNT in common solvents, polydispersity in CNT length and diameter and mixture of metallic and semiconducting CNT^{141, 146, 147}.

On the other hand, graphene, another allotrope of carbon with 2D single sheet of carbon atoms arranged in a hexagonal network (Figure 3.1), has received great attention in recent years due to its unique structure, superior electrical conductivity, high electron mobility, large surface area and high transparency^{148, 149}. Graphene can exhibit a high electron mobility of $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ due to its 2D π - π conjugated network and owing to its large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), it can absorb a high amount of reactants which are

beneficial for enhancing the photocatalytic performances^{149, 150}. Graphene was first discovered in 2004 by Novoselov and Geim via mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite¹⁵¹. Although the discovery of single layer of carbon atoms via mechanical exfoliation has led to extensive research and development of graphene, this method of mechanical exfoliation is not suitable for large quantities production. Thus, several alternative methods have been developed to synthesize graphene and one of the methods involves the oxidization of graphite, subsequent exfoliation and reduction of graphite¹⁵². To oxidize graphite, the most commonly used method is the Hummers method where sulphuric acid is mixed with potassium permanganate to form dimanganeseheptoxide (Mn_2O_7) which is a strong oxidizing agent to oxidize graphite¹⁵³. To exfoliate graphite oxide and form graphene oxide (GO), a variety of thermal and mechanical methods can be used and the most common method is sonicating and/or stirring GO in water or polar organic media¹⁵⁴. To reduce GO, several reducing agents such as hydrazine hydrate¹⁵⁵, lithium aluminium hydride¹⁵⁶ and sodium borohydride¹⁵⁷ can be used and hydrazine hydrate is found to be the best in producing very thin graphene-like sheets¹⁵⁵.

Figure 3.1 Graphene, an atomic layer of C atoms arranged in honeycomb structure.

By coupling TiO_2 with rGO, researchers reported that rGO- TiO_2 (P25) composites showed enhanced photocatalytic activities as compared to TiO_2 alone^{148, 149} due to effective charge separation. However, most of rGO- TiO_2 composites reported are anatase, rutile or anatase/rutile TiO_2 with rGO^{148, 149, 158-161} and there has been no report on the photocatalytic performance using composite between two-phase anatase/brookite and graphene. Our intention is to further enhance the photocatalytic activity of our as-synthesized two-phase anatase/brookite TiO_2 by improving the charge separation via coupling with a good electron transport layer such as graphene. Herein, we synthesized rGO-anatase/brookite TiO_2 mixtures via chemical reduction of GO. GO was synthesized via Hummers method and dispersed in suspension with two-phase anatase/brookite TiO_2 . Subsequently, GO was reduced to rGO with hydrazine hydrate forming rGO-anatase/brookite TiO_2 mixtures.

3.2 Experimental Section

3.2.1 Hydrothermal Synthesis of Anatase/Brookite TiO₂

The hydrothermal synthesis of two-phase anatase/brookite TiO₂ follows the same procedure described earlier (Section 2.2.1) with heating temperature of 200 °C and reaction time of 14 hours.

3.2.2 Synthesis of Graphene Oxide via Hummers Method

1 g of pure graphite flakes (Sigma Aldrich) was added into the mixture of 0.75 g of NaNO₃ (Sigma Aldrich) and 34 mL of H₂SO₄ (Sigma Aldrich) which was subsequently stirred vigorously and kept in an ice bath. 5 g of KMnO₄ was added into the solution slowly and the temperature of the solution was increased and maintained at 35 °C. The solution was stirred for 2 hours and 50 mL of DI water was added. 4 mL of 30 % of H₂O₂ was added dropwise into the solution and a yellow solution was formed along with bubbling. The mixture was filtered and washed with 1:10 HCl aqueous solution followed by a large amount of deionized water to reach pH 7. Subsequently, the suspension was sonicated for 5 hours and centrifuged to collect a stable GO solution from the supernatant.

3.2.3 Synthesis of rGO-Anatase/Brookite TiO₂

Different wt% of GO (1 wt%, 2 wt% and 5 wt%) were mixed with the as-synthesized two-phase anatase/brookite TiO₂ in a suspension. The suspension was sonicated for 30

minutes and 1 ml of hydrazine hydrate was added. The mixture was stirred at 1000 rpm for 10 hours. The resulting powders were collected via centrifugation, washed with deionized water and dried at 80 °C. The powders were heat treated in air at 400 °C for 2 hours with a ramping rate of 5 °C per min. 400 °C was chosen because higher the heat treatment temperature, it would decrease the surface area of TiO_2 ¹⁶² while a low heat treatment temperature such as 300 °C is not sufficient for good interfacial contact between anatase/brookite TiO_2 and rGO. In comparison with heat treatment temperature of 300 °C and 400 °C, anatase/brookite TiO_2 and rGO mixture heat treated at 400 °C produces higher amount of H_2 (not shown in this thesis) and thus a moderate high temperature of 400 °C was chosen as the heat treatment temperature. Similarly, 2 wt% of GO was mixed with P25 (Degussa) with the same preparation procedure to obtain rGO-anatase/rutile TiO_2 mixture. Two-phase anatase/brookite TiO_2 without the addition of GO was heat treated in air 400 °C for 2 hours.

3.2.4 Characterization

The XRD patterns, FESEM and TEM images and PL spectra were collected using the same equipment described in Section 2.2.3. Raman spectroscopy was performed on a WITec $\alpha 300\text{S.R}$ spectrometer (WITec Instrument Corp, Germany) with laser wavelength of 488 nm at room temperature.

3.2.5 Evaluation of Photocatalytic Activity

The photocatalytic hydrogen production experiment follows the same procedure described earlier (Section 2.2.6). 45 mg of rGO-anatase/brookite TiO_2 was suspended in aqueous methanol solution (20 vol %) in the glass reactor with stirring. 0.3 wt% of Pt was loaded on the rGO-anatase/brookite TiO_2 mixture via photodeposition. The required amount of H_2PtCl_6 was added in the reactant solution and the reactor was irradiated from the top with UV-Vis light with intensity of 230 mW cm^{-2} for 2 hours. Subsequently, the reactant solution was evacuated several times to remove air completely and irradiated with UV-Vis light.

3.3 Results and Discussion

3.3.1 Materials Characterization of rGO-Anatase/Brookite TiO_2 Mixture

A series of rGO-anatase/brookite TiO_2 mixtures denote $\text{G}_x\text{-AB}$ where x stands for the wt% of GO added to the two-phase anatase/brookite TiO_2 before the reduction process of GO with hydrazine hydrate while two-phase anatase/brookite TiO_2 denote AB. P25 with 2 wt% of GO is denoted as $\text{G}_2\text{-P25}$. Two-phase anatase/brookite TiO_2 is denoted as AB and two-phase anatase/brookite TiO_2 heated treated at 400°C is denoted as AB-HT. Figure 3.2 shows the XRD patterns of $\text{G}_1\text{-AB}$, $\text{G}_2\text{-AB}$ and $\text{G}_5\text{-AB}$ samples with 1 wt%, 2 wt% and 5 wt% of GO respectively. From the diffraction patterns, two-phase anatase/brookite TiO_2 is evidenced to be present. On the other hand, no graphene diffraction peak is observed which could be due to the main characteristic peak of graphene at 25.4° is shielded by the strong intensity diffraction peaks from anatase (101) and brookite (120) planes.

Figure 3.2 XRD patterns of G₁-AB, G₂-AB and G₅-AB. Symbol ^a and * denote anatase (JCPDS 21-1272) and brookite (JCPDS 29-1360) respectively.

Thus, to prove the presence of rGO in rGO-anatase/brookite TiO₂ mixtures, Raman spectroscopy was employed. Figure 3.3 shows the Raman spectra of graphene oxide (GO), rGO-anatase/brookite TiO₂ composite (G₁-AB) and two-phase anatase/brookite TiO₂ (AB). In the Raman spectra of two-phase anatase/brookite TiO₂, vibration peaks are observed at 314 cm⁻¹, 388 cm⁻¹, 507 cm⁻¹ and 630 cm⁻¹ which are the characteristics B_{1g} mode of brookite phase, B_{1g}, A_{1g} and E_g modes of anatase phase respectively ¹⁶³. Graphene has two typical peaks at 1346 cm⁻¹ and 1586 cm⁻¹ corresponding to the D (disorder) and G (graphitic) bands. The D band arises from the disruption of the symmetrical hexagonal graphitic lattice caused by internal structural defects, edge defects

and dangling bonds while the G band arises from the in-plane vibration of symmetric sp^2 bonded carbon atoms^{148, 164, 165}. For the G_1 -AB sample, the anatase, brookite and graphene bands are observed indicating the presence of rGO in rGO-anatase/brookite TiO_2 mixture. Moreover, the rGO-anatase/brookite TiO_2 mixture shows an increased D/G intensity ratio as compared to GO which suggests a decrease in the average size of the in-plane sp^2 domains upon reduction of the exfoliated GO and thus confirming the existence of rGO sheets in the rGO-anatase/brookite TiO_2 mixture^{148, 165}.

Figure 3.3 Raman spectra of GO, G_1 -AB and AB. Inset shows the D and G bands of GO and G_1 -AB.

The morphology of the rGO-TiO₂ mixtures was characterized via FESEM and TEM as shown in Figure 3.4. As observed, the rGO sheets are decorated with nanoparticles and nanoplates. As discussed in Chapter 2, anatase TiO₂ and brookite TiO₂ were in the form of nanoparticles and nanoplates. Thus, the nanoparticles and nanoplates observed are anatase and brookite TiO₂ while the flat nanosheets are rGO. The size of the rGO sheets are less than 200 nm in length. Figure 3.4d and Figure 3.4e show the TEM images of 0.3 wt% Pt loaded G₂-AB and as observed, Pt cocatalyst was loaded on anatase/brookite TiO₂ and as well as on rGO.

Figure 3.4 a) FESEM images of G₅-AB, TEM images of b, c) G₅-AB and d, e) 0.3 wt% Pt loaded G₂-AB.

Table 3.1 shows the specific surface areas of AB, AB-HT, G₁-AB, G₂-AB, G₅-AB and G₂-P25. With heat treatment at 400 °C, the surface area of two-phase anatase/brookite TiO₂ (AB-HT) decreases from 23.77 m² g⁻¹ to 9.11 m² g⁻¹. In comparison with AB-HT as the rGO-anatase/brookite TiO₂ mixtures were heat treated for good interfacial contact, with the addition of rGO, the surface area of the rGO-anatase/brookite TiO₂ mixtures increases. This is due to the nanosheet structure of rGO as observed in FESEM and TEM images in Figure 3.4 which results in large surface area. With the increase in surface area, it is beneficial in enhancing the photocatalytic activity as it provides a larger area to absorb a higher amount of reactants. However, adding excessive amount of rGO may not be helpful as it may block the light absorption of the photoactive material and will be discussed later.

Table 3.1 BET surface areas of AB, AB-HT G₁-AB, G₂-AB, G₅-AB and G₂-P25.

Sample	BET Surface Area (m ² g ⁻¹)
AB	23.77
AB-HT	9.11
G ₁ -AB	19.87
G ₂ -AB	29.73
G ₅ -AB	24.77
G ₂ -P25	36.87

3.3.2 Hydrogen Production via Photocatalytic Water Splitting with rGO-Anatase/Brookite TiO₂ Mixtures

The amount of hydrogen evolved per gram of catalyst per hour in aqueous methanol solution over 0.3 wt% Pt loaded photocatalyst under UV-Vis light illumination is presented in Figure 3.5. With the addition of rGO (G₁-AB, G₂-AB and G₅-AB), the H₂ evolution increases as compared to two-phase anatase/brookite TiO₂ (AB and AB-HT). The H₂ evolution increased by 80% with sample G₂-AB as compared to AB. The amount of H₂ produced with AB photocatalyst is lower than the H₂ produced with the two-phase anatase/brookite TiO₂ as discussed in Section 2.3.5 with the same synthesis method and conditions. This could be due to the light source degradation and lower light intensity which results in lower H₂ yield. To prove that the improvement of H₂ production with rGO-anatase/brookite TiO₂ mixture is mainly contributed by the effect of addition of rGO and not due to the improved crystallinity of anatase/brookite TiO₂ by heat treatment, H₂ production from AB and AB-HT were compared. From Figure 3.5, with heat treatment of the two-phase anatase/brookite TiO₂, the amount of H₂ generated is lower which could be due to decrease in surface area (Table 3.1).

The great enhancement in hydrogen yield is proven to be due to more effective charge separation with the presence of rGO. When UV-Vis light is illuminated on the rGO-anatase/brookite TiO₂, electrons from both brookite and anatase TiO₂ are photoexcited creating electron-hole pairs. The photogenerated electrons from brookite could be transferred to anatase to suppress electron-hole recombination. Moreover, with the addition of rGO, electrons could be further transferred from anatase TiO₂ to rGO and brookite TiO₂ to rGO. The work function of graphene is reported to be 4.42 eV¹⁶⁶ while

the conduction band position of anatase TiO_2 is 4.21 eV with vacuum level as reference¹⁶⁷, thus graphene can accept electrons from anatase and brookite TiO_2 with brookite conduction band more cathodic than anatase conduction band (Figure 3.6a and Figure 3.6b). However, since photogenerated electrons could be transferred from brookite to rGO, brookite to anatase and to rGO, and anatase to rGO, one of the concerns would be which electron transfer process would be the dominant and effective charge separation process. McDaniel et. al reported with a smaller conduction band offset, it results in shorter charge separation time across the heterojunction¹⁶⁸. Thus to confirm the dominant charge transfer process, photoluminescence (PL) emission spectroscopic study was carried out and shown in the next section. As a result, inhibition of electron-hole recombination is further enhanced and thus leading to enhanced photocatalytic activity. Moreover, with the addition of rGO, the surface area of the rGO-anatase/brookite TiO_2 composite increases which also leads to the enhancement of photocatalytic activity.

However, with further increment of the GO amount to 5 wt%, the H_2 evolution decreases as compared to 2 wt% of GO. This could be due to rGO “shielding effect” where a high concentration of rGO will cause the rGO-anatase/brookite TiO_2 mixture to have a darker and more opaque color which will reduce the light absorption on the TiO_2 surface and thus leading to a reduction in photocatalytic activity¹⁴⁸ (see Figure 3.7. for the photos of $\text{G}_1\text{-AB}$, $\text{G}_2\text{-AB}$ and $\text{G}_5\text{-AB}$ samples). Hence, with 2 wt% of GO added to two phase anatase/brookite TiO_2 before chemical reduction of GO, the amount of H_2 produced is the highest with $3051 \mu\text{mole g}^{-1} \text{h}^{-1}$ as compared with 1 wt% and 5 wt% of GO.

Another important consideration semiconductor composite is the conduction band potential of all the constituent phase. In comparison of P25 with 2wt% of GO (G₂-P25), G₂-AB produces 2.3 times the amount of H₂ produced by G₂-P25 despite G₂-P25 has higher surface area as shown in Table 3.1. The higher photocatalytic activity of G₂-AB which consists of anatase/brookite TiO₂ over G₂-P25 with anatase/rutile TiO₂ is attributed to the higher cathodic potential of brookite conduction band than anatase and rutile conduction bands which energetically favors the reduction of protons to produce H₂. In addition, the conduction band potential of rutile is less cathodic than the chemical potential for water reduction and thus it cannot participate in water reduction (Figure 3.6a)^{124, 125}. Hence, under UV-Vis illumination, both photogenerated electrons in the brookite and anatase phase in G₂-AB are able to reduce protons to H₂ and electrons from brookite conduction band can be transferred to the anatase conduction band. With the addition of rGO, the photogenerated electrons from brookite phase can be further transferred to rGO and as well as the electrons from the anatase phase can be transferred to rGO for effective charge separation (Figure 3.6b). On the other hand, for G₂-P25 sample, under UV-Vis illumination, only the photogenerated electrons in the anatase phase and electrons transferred to rGO from anatase are able to reduce water to form H₂. The electrons that are either generated on rutile or transferred from anatase are not energetically favourable for hydrogen production. This can be proven from Figure 3.8 which shows the comparison of H₂ production with G₂-P25 and G₂-A. With the presence of rutile phase, G₂-P25 produces lower amount of H₂ than G₂-A despite G₂-A has slightly lower or almost the same surface area (36.16 m² g⁻¹) as G₂-P25 (36.87 m² g⁻¹). Therefore, despite that the addition of rGO can help to inhibit electron-hole recombination, some of

the electrons in the rutile phases of G₂-P25 do not contribute to hydrogen yield. As a result, the photocatalytic activity of our rGO-anatase/brookite TiO₂ composite is better than G₂-P25 composite.

Figure 3.5 Hydrogen evolved per gram of catalyst per hour under UV-Vis irradiation in aqueous methanol solution over 0.3 wt% Pt loaded photocatalysts; AB, AB-HT, G₁-AB, G₂-AB, G₅-AB, G₂-P25.

b)

Figure 3.6 a) Band diagram of brookite, anatase, rutile TiO_2 and graphene relative to redox potential of water at pH 7^{21, 125, 139, 169}. b) Schematic diagram of the electron transfer in rGO-anatase/brookite TiO_2 mixture under UV-Vis light illumination.

Figure 3.7 Photos of G₁-AB, G₂-AB and G₅-AB samples.

Figure 3.8 Hydrogen evolved per gram of catalyst per hour under UV-Vis irradiation in aqueous methanol solution over 0.3 wt% Pt loaded of G₂-P25 and G₂-A photocatalysts.

3.3.3 Photoluminescence of rGO-Anatase/Brookite TiO₂ Mixtures

Photoluminescence (PL) emission spectroscopy is employed to study the recombination behavior of the photogenerated electrons and holes in rGO-anatase/brookite TiO₂ mixtures. Figure 3.9 shows the PL spectra for AB-HT, G₁-AB, G₂-AB and G₅-AB. of PL spectra. PL spectra of 2 wt% of rGO with anatase and 2 wt% of rGO with brookite were included in Figure 3.9 which are denoted as G₂-A and G₂-B respectively. The peak at 378 nm corresponding to 3.28 eV, is ascribed to direct electron-hole recombination in anatase and brookite TiO₂ which possess a band gap of 3.2 eV and 3.3 eV respectively. The emission band from 400 to 500 nm corresponding to 3.10 to 2.48 eV arises from TiO₂ indirect band gap and surface recombination processes^{139, 140}. With the addition of rGO, the PL intensity of G₁-AB, G₂-AB and G₅-AB are much lower than AB-HT indicating the diminution of the electron and hole recombination process which is due to the charge transfer from brookite and anatase TiO₂ to rGO leading to effective charge separation. As a result, the H₂ evolution is enhanced with the addition of rGO with anatase/brookite TiO₂.

To determine the most effective and dominant charge transfer process in the two-phase anatase/brookite-rGO mixture, PL intensity of G₂-A, G₂-B and G₂-AB are compared. From Figure 3.9, G₂-B has higher PL intensity than G₂-A which could be due to the larger potential offset of brookite and rGO conduction band potential than anatase and rGO conduction band potential as shown in Figure 3.6a which results in less effective electron transfer from brookite to rGO than anatase to rGO¹⁶⁸. With two-phase anatase/brookite, the PL intensity is the lowest with G₂-AB than G₂-A and G₂-B, this indicates that electron

transfer from brookite to anatase and to rGO could be the most effective and dominant charge separation process leading to the enhancement of H_2 generation.

Figure 3.9 Photoluminescence spectra of AB-HT, G_1 -AB, G_2 -AB, G_5 -AB, G_2 -A and G_2 -B.

3.4 Conclusions for the Chapter

In summary, a series of rGO-anatase/brookite TiO_2 mixtures with enhanced photocatalytic H_2 production were synthesized via hydrothermal synthesis of two-phase anatase/brookite TiO_2 and chemical reduction of GO. Results have shown that with the addition of rGO, the H_2 evolution is higher with rGO-anatase/brookite TiO_2 mixture as compared to anatase/brookite TiO_2 without rGO. From PL analysis, it is proven that the

probability of electron-hole recombination is lower with the addition of rGO as rGO sheets acting as electron collector to separate the photogenerated charge carriers and the electron transfer from brookite to anatase and to rGO is the most effective and dominant charge separation process. Furthermore, with the addition of rGO, surface area of rGO-anatase/brookite TiO_2 composite increases which could also lead to enhanced photocatalytic activity. The optimal weight percentage of GO in the rGO-anatase/brookite TiO_2 mixture was found to be 2 wt%, producing a rate of $3051 \mu\text{mole g}^{-1} \text{h}^{-1}$ of H_2 under UV-Vis illumination which is higher than the H_2 production from 2 wt% of GO with P25. This is attributed to the higher cathodic potential of brookite conduction band as compared to anatase and rutile conduction bands leading to higher reduction power to reduce water to produce H_2 . Overall, the H_2 production is enhanced due to the synergistic effects of improved electron-hole separation, higher surface area and higher reduction power to reduce water with rGO-anatase/brookite TiO_2 mixture.

However, TiO_2 is a wide band gap semiconductor which is only active under UV illumination. For visible light harvesting and enhancing the solar to hydrogen conversion efficiency, g- C_3N_4 which is visible light active is coupled with the two-phase anatase/brookite TiO_2 in order to generate hydrogen via photocatalytic water splitting under visible light irradiation. This will be discussed in the next chapter.

Chapter 4: Enhanced Visible Light Hydrogen Production with Hydrogenated g-C₃N₄ on Two-phase Anatase/Brookite TiO₂ Heterostructure

4.1 Introduction

As discussed earlier in the previous chapters, wide band gap TiO₂ is only photo-active to UV light. As UV light is only 5% of the solar spectrum, TiO₂ photocatalysts produce H₂ with low solar to hydrogen conversion efficiency. Therefore, to improve the solar to hydrogen conversion efficiency, one of the effective methods to enable visible light harvesting is to couple TiO₂ with secondary semiconductor which is visible light active. Moreover, by coupling TiO₂ with another semiconductor, it creates a heterojunction which helps in overcoming the fast recombination of the photogenerated electrons and holes.

Recently, metal-free and graphite-like carbon nitride (g-C₃N₄) based on tri-s-triazine (heptazine) units has received much attention in the photocatalysts field due to its low cost, good stability and its excellent optical and electronics properties¹⁷⁰. Carbon nitride was first synthesized in polymeric form by Berzelius and given the name “melon” by Liebig in 1834¹⁷¹. It is regarded as one of the oldest synthetic polymers reported. Carbon nitrides can exist in several allotropes and graphitic carbon nitride (g-C₃N₄) is the most stable allotrope under ambient conditions¹⁷². g-C₃N₄ has band gap energy of 2.7 eV which is able to absorb light up to 450 nm and its conduction and valence bands are

cathodically and anodically sufficient for water reduction and oxidation respectively to produce hydrogen¹⁷². In particular, the conduction band potential of g-C₃N₄ is attractive to the photocatalytic reduction reaction such as hydrogen evolution^{172, 173}. g-C₃N₄ is mainly composed of carbon and nitrogen and thus it is easy to modify its reactivity without major changes in its overall composition by organic chemistry^{174, 175}. In addition, g-C₃N₄ exhibits high stability under light illumination in acidic or basic solution due to the strong covalent bonds between carbon and nitride atoms^{176, 177}. Over the years, g-C₃N₄ has been synthesized with a wide range of carbon- and nitrogen-rich precursors giving different properties such as surface area, porosity, band gap, and photocatalytic activity due to different tectonic units, reaction pathways and degree of polymerization¹⁷⁰. Montigaud et al. reported the synthesis of g-C₃N₄ based on the condensation of s-triazine rings with melamine and cyanuric chloride at 250 °C with triethylamine acting as solvent in supercritical conditions¹⁷⁸. Wirnhier et al. synthesized 2D g-C₃N₄ based on imide-linked triazine units via ionothermal synthesis with temperature-induced condensation of dicyandiamide in a eutectic mixture of lithium chloride and potassium chloride as solvent¹⁷⁹. g-C₃N₄ based on the condensation of tri-s-triazine rings (heptazine) were reported to form from the thermal condensation of cyanamide^{180, 181}, dicyandiamide^{172, 182} and melamine^{183, 184}. g-C₃N₄ synthesized based on triazine and tri-s-triazine tectonic units have different stability due to different N atom electronic environment and sizes of the nitride pores as shown in Figure 4.1¹⁸⁵. Kroke et al. calculated that g-C₃N₄ with tri-s-triazine tectonic units is 30 kJ mol⁻¹ more stable than with triazine tectonic units based on density-functional theory (DFT)¹⁸⁶.

Thus, to obtain the tri-s-triazine structure, dicyandiamide was chosen as the precursor to synthesize $\text{g-C}_3\text{N}_4$ in this study. Moreover, instead of the usual heating of dicyandiamide in static air or in N_2 at $550\text{ }^\circ\text{C}$, we synthesized $\text{g-C}_3\text{N}_4$ with the introduction of H_2 gas during the heat treatment process of dicyandiamide where dark yellow $\text{g-C}_3\text{N}_4$ and brown $\text{g-C}_3\text{N}_4$ were formed with the introduction of forming gas (5% H_2 with 95% Ar) and pure H_2 gas respectively. From detailed investigation on the chemical, optical and electronic properties of the samples, with the introduction of H_2 gas during the heat treatment process of dicyandiamide, nitrogen vacancy (V_N) and hydrogen substitution at nitrogen vacancy (H_N) in $\text{g-C}_3\text{N}_4$ were created. This defective $\text{g-C}_3\text{N}_4$ was found to produce higher amount of H_2 than the pristine $\text{g-C}_3\text{N}_4$. To couple the defective $\text{g-C}_3\text{N}_4$ with two-phase anatase/brookite TiO_2 , $\text{g-C}_3\text{N}_4$ was horizontally ball-milled with two-phase anatase/brookite TiO_2 in suspension to ensure a homogenous mixture. The mixture was subsequently heated treated to ensure a good interfacial contact. Although there are papers reporting the enhancement of H_2 production with $\text{g-C}_3\text{N}_4/\text{TiO}_2$ mixture, the TiO_2 reported is a single phase anatase TiO_2 or anatase/rutile TiO_2 ^{35, 173, 177, 187}. In this study, H-doped $\text{g-C}_3\text{N}_4$ with two-phase anatase/brookite TiO_2 were synthesized and results have shown that H_2 production is greatly enhanced under visible light irradiation with H-doped $\text{g-C}_3\text{N}_4$ -anatase/brookite TiO_2 mixture as compared to pristine $\text{g-C}_3\text{N}_4$.

Figure 4.1 s-Triazine (left) and tri-s-triazine (right) tectonic units of g-C₃N₄.

4.2 Experimental Section

4.2.1 Sample Preparation

g-C₃N₄ was synthesized by heating 2 g of dicyandiamide (Sigma Aldrich) in a crucible at 550 °C for 4 hours in air, N₂, forming gas (5% H₂ with 95% Ar) and pure H₂ gas respectively with a ramping rate of 2 °C min⁻¹. The agglomerates were then grinded into powder with mortar and pestle. It should be taken note that the “g-C₃N₄” term used here refers to the product formed by the condensation of dicyandiamide so as to be consistent with the widely used “g-C₃N₄” in the literature which is actually non-stoichiometric.

Two-phase anatase/brookite TiO₂ (88 wt% of anatase with 12 wt% of brookite) was synthesized with the same hydrothermal synthesis procedure described earlier (Section 2.2.1) with heating temperature of 200 °C and reaction time of 14 hours. For comparison,

pure anatase and brookite were synthesized with 0.5 M and 1.2 M of NaOH at 200 °C for 24 hours respectively. Rutile TiO₂ was obtained by heating treating the two-phase anatase/brookite TiO₂ at 950 °C for 1 hour to convert the anatase and brookite phases to rutile.

Different amounts of g-C₃N₄ and two-phase anatase/brookite TiO₂ were added in 5 ml of ethanol and the mixture was ball-milled horizontally for 1 hour with a rotation speed of 950 rpm to have a homogenous mixture. The mixture was then collected via centrifugation, washed with deionized water and dried at 80 °C. Subsequently, the g-C₃N₄/anatase/brookite TiO₂ mixture was heated at 450 °C for 2 hours in air for better interfacial contact. Similarly, g-C₃N₄ was ball milled with pure anatase or brookite or P25 and heat treated for comparison. For g-C₃N₄ with three phases of TiO₂, g-C₃N₄ was ball milled and heat treated with rutile and two-phase anatase/brookite TiO₂.

4.2.2 Characterization

The XRD patterns, FESEM and TEM images, surface areas, optical diffuse reflectance and PL spectra with excitation wavelength of 400 nm were collected using the same equipment described in Section 2.2.3. Fourier transform infrared (FT-IR) spectra were collected on PerkinElmer FT-IR/NIR spectrometer with KBr as reference sample. X-ray photoelectron spectroscopy (XPS) analysis was performed on a self-assembled x-ray photoelectron spectrometer with monochromatic Al-K α (h ν =1486.7eV) which was used at 300W, 14kV and the binding energies were calibrated using the C 1s peak at 284.6 eV. Elemental analysis for carbon and nitrogen were performed on a Vario EL III Element

analyzer. Thickness of the g-C₃N₄ sheets was determined by measuring the height difference between two layers from topographic images obtained from Digital Instruments 3100 atomic force microscopy (AFM).

4.2.3 Density Functional Theory Based Electronic Structure Modeling

All calculations were carried out using CASTEP¹⁸⁸, as implemented in Materials Studio 5.0. We selected the reported structure of g-C₃N₄ (P $\bar{6}$ m2)^{189, 190}, as a starting structure. A complete geometry optimization of the lattice, including lattice parameters and fractional coordinates of the atoms was performed on the pristine structures. Using the optimized supercell, one N vacancy and one H substitution at N site was created and the defect structures were further optimized. The exchange-correlation functional was constructed by the Generalized Gradient Approximations (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE). An energy cutoff of 400 eV and a Monkhorst–Pack k-points mesh of 3×3×3 was found sufficient for geometry optimization of 2×2×1 supercell. The forces on individual ions in the optimized structure were below 0.03 eV Å⁻¹. Plots of partial and total density of states (DOS) and optical absorption spectra of the perfect and the defect structures were compared. Band alignment of defect g-C₃N₄ systems was derived from the DOS plots.

4.2.4 Evaluation of Photocatalytic Activity

The photocatalytic hydrogen production experiment follows the same procedure described earlier (Section 2.2.6). 45 mg of photocatalyst was suspended in 100 mL of triethanolamine (Sigma Aldrich) aqueous solution (20 vol%) in the glass reactor with stirring. 1.0 wt% of Pt was loaded on the photocatalyst particles via photodeposition. (1 wt% of Pt was chosen because a comparison of H_2 produced with 0.3 wt% Pt, 1 wt% Pt and 3 wt% Pt loaded g- C_3N_4 was carried out (not shown in this thesis) and 1 wt% Pt loaded g- C_3N_4 produces the highest of H_2 under visible light irradiation). The required amount of H_2PtCl_6 was added in the reactant solution and the reactor was irradiated from the top with UV-Vis light with intensity of 215 mW cm^{-2} for 2 hours. Subsequently, the reactant solution was evacuated several times to remove air completely and irradiated with visible light (420 nm cut-off filter) with light intensity of 100 mW cm^{-2} . The amount of generated H_2 gas was quantitatively analyzed every 2 h by a gas chromatograph

4.3 Results and Discussion

4.3.1 H-doped g- C_3N_4

4.3.1.1 Crystal Structure and Chemical State of H-doped g- C_3N_4

g- C_3N_4 synthesized in air, N_2 , forming gas and pure H_2 are named as g- C_3N_4 (air), g- C_3N_4 (N_2), g- C_3N_4 (forming) and g- C_3N_4 (H_2) respectively in this report. The XRD patterns of g- C_3N_4 (air), g- C_3N_4 (N_2), g- C_3N_4 (forming) and g- C_3N_4 (H_2) are presented in Figure 4.2. These four samples all show graphite-like C_3N_4 structure with two distinctive peaks at 13.1° and 27.4° . The peak at 13.1° corresponds to the in-plane structural

packing motif of tri-s-triazine units ¹⁹¹ while the peak at 27.4° originates from the interplanar stacking of the conjugated aromatic system with a distance of 0.326 nm similar to the graphite layer structure ¹⁷². The formation of g-C₃N₄ in the four samples is further confirmed by the FT-IR spectra shown in Figure 4.3. The absorption band at 803 cm⁻¹ corresponds to the breathing mode of the triazine units. Absorption bands at 1240, 1322 and 1411 cm⁻¹ correspond to the aromatic C-N vibrations while absorption bands at 1563 and 1649 cm⁻¹ correspond to the C=N vibrations. The broad band in the range of 3000 to 3500 cm⁻¹ can be assigned to the adsorbed water molecules and the uncondensed amine groups ^{177, 191}.

Figure 4.2 XRD patterns of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂).

Figure 4.3 FT-IR spectra of $\text{g-C}_3\text{N}_4$ (air), $\text{g-C}_3\text{N}_4$ (N_2), $\text{g-C}_3\text{N}_4$ (forming) and $\text{g-C}_3\text{N}_4$ (H_2).

4.3.1.2 Optical Properties of H-doped $\text{g-C}_3\text{N}_4$

Figure 4.4a shows the UV-Vis diffuse reflectance spectra and the inset shows the photographs of the $\text{g-C}_3\text{N}_4$ (air), $\text{g-C}_3\text{N}_4$ (N_2), $\text{g-C}_3\text{N}_4$ (forming) and $\text{g-C}_3\text{N}_4$ (H_2) samples and Figure 4.4b shows the Kubelka Munk plots to determine the band gaps of $\text{g-C}_3\text{N}_4$ (air), $\text{g-C}_3\text{N}_4$ (N_2), $\text{g-C}_3\text{N}_4$ (forming) and $\text{g-C}_3\text{N}_4$ (H_2). As observed, $\text{g-C}_3\text{N}_4$ (air) is pale yellow in color and has a band gap of 2.74 eV while for $\text{g-C}_3\text{N}_4$ (N_2) and $\text{g-C}_3\text{N}_4$ (forming), it is darker in color and there is a red shift of the adsorption edge with lower band gap energy of 2.67 eV. When heated in pure H_2 , the $\text{g-C}_3\text{N}_4$ obtained is brown in color with absorption extending up to 700 nm and has band gap of 2.0 eV. Hence, heating in different gas environment will result in different electronic band structure of the $\text{g-C}_3\text{N}_4$.

Figure 4.4 a) UV-Vis diffuse reflectance spectra of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂). Insets show the photographs of the photocatalyst. b) Kubelka Munk plots of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂), showing fits to obtain the band gaps.

4.3.1.3 Chemical Structure of H-doped g-C₃N₄

In order to investigate the shift in the absorption, difference in the band structure and the atomic structure changes, XPS was used to determine the chemical states of carbon and nitrogen as shown in Figure 4.5. Typical g-C₃N₄ XPS C 1s spectrum can be deconvoluted into two peaks with binding energies of 288 eV and 284.6 eV. The peak at 288 eV is identified as sp² bonded C atoms in aromatic ring bonded to three N atoms (three-coordinated C atoms, C_{3c}, as shown in Figure 4.6) while the peak at 284.6 eV is assigned as the graphitic carbon C=C (284.6 eV), C-C (284.7 eV) and as well as adventitious carbon adsorbed on the surface¹⁹¹⁻¹⁹³. All three samples, g-C₃N₄ (air), g-

$C_3N_4(N_2)$ and $g-C_3N_4$ (forming), have the typical $g-C_3N_4$ C 1s spectrum with two peaks at 288 eV and 284.6 eV whereas for the $g-C_3N_4(H_2)$, the C 1s spectrum shows three peaks at 284.6 eV, 287.3 eV and 290.6 eV as shown in Figure 4.5a. The additional peak at 290.6 eV is attributed to the two-coordinated C atoms (C_{2c}) which arises due to the loss of N atoms resulting in the formation of C_{2c} from the three-coordinated carbon C_{3c} as shown in Figure 4.6. Niu. et al. reported the presence of nitrogen vacancies in $g-C_3N_4$ with higher synthesis temperature of 600 °C which as a result leads to the formation of two-coordinated C atoms¹⁹². The additional C_{2c} peak is not observed in the $g-C_3N_4$ (forming) sample which could be due to the low number of N vacancies as a result of low percentage of H_2 in the forming gas but from the N 1s spectrum, N vacancies are evidenced to be formed in $g-C_3N_4$ (forming) sample which will be explained later. In addition, due to the reducing effect of H_2 gas, large amount of graphitic carbon and adventitious carbon are removed leading to the decrease in normalized intensity of the 284.6 eV peak for the $g-C_3N_4(H_2)$ sample.

Typical $g-C_3N_4$ XPS N 1s spectrum can be deconvoluted into three peaks with binding energies of 399.6 eV, 398.2 eV and 397.5 eV. The peaks at 397.5 eV and 398.2 eV are ascribed to the two-coordinated N atoms (C-N-C) and three-coordinated N atoms (N-(C)₃) in the heptazine unit framework which are denoted N_{2c} and N_{3c} in Figure 4.6 respectively while the peak at 399.6 eV is attributed to the N atoms bonded to H (N-H)¹⁹¹. From Figure 4.5b, $g-C_3N_4$ (air) and $g-C_3N_4(N_2)$ samples have the typical C_3N_4 N 1s spectrum while for $g-C_3N_4$ (forming) sample, there is a slight shift of the two-coordinated N, three-coordinated N and N bonded to H peaks towards lower binding energy. Nevertheless, the relative position of the three peaks with respect to each other is the

same as compared to g-C₃N₄ (air) and g-C₃N₄ (N₂) samples as shown in Figure 4.7. The relative peak position of the N 1s spectrum as shown in Figure 4.7 was obtained by fixing peak 1 of the four samples at a fixed binding energy. The relative position of peak 1, 2 and 3 with respect to each other are similar for the g-C₃N₄ (air), g-C₃N₄ (N₂) and g-C₃N₄ (forming) samples. The binding energy difference between peak 1 and peak 2 is approximately 0.7 eV and binding energy difference between peak 2 and peak 3 is approximately 1.4 eV which are similar to the binding energy difference between two-coordinated N peak and three-coordinated N peak and the binding energy difference between three-coordinated N peak and N bonded to H peak respectively. As a result, peak 1, 2 and 3 for the g-C₃N₄ (air), g-C₃N₄ (N₂) and g-C₃N₄ (forming) samples can be further confirmed to be assigned to the two-coordinated N, three-coordinated N and N bonded to H peaks. For the g-C₃N₄ (H₂) sample, the binding energy difference between peak 1 and peak 2 is 2.4 eV which is approximately similar to the binding energy difference of 2.1 eV between the two-coordinated N peak and N bonded to H peak. Thus, peak 1 and 2 of the g-C₃N₄ (H₂) sample can be assigned to the two-coordinated N peak and N bonded to H peak while the three-coordinated N peak could be overlapped by either the two-coordinated N peak or N bonded to H peak. This is due to the low peak intensity where only two peaks instead of three can be deconvolved in the binding energy range from peak 1 to 2. Peak 3 of the g-C₃N₄ (H₂) sample is attributed to the charging effects^{185, 193}.

Comparing the peak area ratio of two-coordinated N to three-coordinated N peak (N_{2c}/N_{3c}) in Figure 4.5b, the peak ratio decreases with g-C₃N₄ (forming) sample as compared to g-C₃N₄ (air) and g-C₃N₄ (N₂) samples indicating the loss of N atoms at the N_{2c} lattice sites and not at the N_{3c} lattice sites. With the formation of the two-coordinated

N vacancy, this will result the two-coordinated C atoms to have unbonded electrons and hydrogen atoms could be bonded to these C atoms giving rise to the increase of C/H atomic ratios which is evidenced by elemental analysis.

Figure 4.5 Deconvoluted high-resolution a) C 1s and b) N 1s XPS spectra of $g\text{-C}_3\text{N}_4$ (air), $g\text{-C}_3\text{N}_4$ (N_2), $g\text{-C}_3\text{N}_4$ (forming) and $g\text{-C}_3\text{N}_4$ (H_2).

Figure 4.6 (Left) Single formula unit of melon with 18 carbon atoms, 27 nitrogen atoms and 9 hydrogen atoms. Two-coordinated nitrogen, three-coordinated nitrogen and three-

coordinated carbon are labeled as N_{2c} , N_{3c} , and C_{3c} respectively. (Right) With the formation of nitrogen vacancy at the N_{2c} lattice site, three-coordinated carbon transforms into two-coordinated carbon with unbonded electrons, C_{2c} . Carbon atom with unbonded electron could react with H atoms to form C-H bond.

Figure 4.7 Relative peak position of the N 1s spectrum by fixing peak 1 at a fixed binding energy for the $g\text{-C}_3\text{N}_4$ (air), $g\text{-C}_3\text{N}_4$ (N_2), $g\text{-C}_3\text{N}_4$ (forming) and $g\text{-C}_3\text{N}_4$ (H_2) samples.

To further prove the existence of the nitrogen vacancies and the additional hydrogen atoms, elemental analysis was carried out to determine the composition of C, N and H in the synthesized $g\text{-C}_3\text{N}_4$ as shown in Table 4.1. In a single formula unit of melon, there are 18 carbon atoms, 27 nitrogen atoms and 9 hydrogen atoms as shown in Figure 4.6¹⁹⁴. Taking that there are 18 C atoms in a single formula unit of melon, from the C/N and C/H

atomic ratios, there are ca. 27.2 N atoms, 8.11 H atoms and 27.2 N atoms, 9.38 H atoms in a single formula unit of melon for the g-C₃N₄ (air) and g-C₃N₄ (N₂) samples respectively which are close to the theoretical value of N and H atoms. For the g-C₃N₄ (forming) and g-C₃N₄ (H₂) samples, the calculated N atoms are less than the theoretical value and the calculated H atoms are much higher than the theoretical value indicating the presence of N vacancies and additional H atoms.

Table 4.1 Composition (wt%) of C, N and H in g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂) determined by elemental analysis and the calculated number of N and H atoms in a single formula unit of melon.

Sample	N (wt%)	C (wt%)	H (wt%)	C/N atomic ratio	C/H atomic ratio	Number of N atoms	Number of H atoms
g-C ₃ N ₄ (air)	62.94	35.72	1.34	0.662	2.218	27.183	8.115
g-C ₃ N ₄ (N ₂)	62.77	35.68	1.55	0.663	1.919	27.147	9.382
g-C ₃ N ₄ (forming)	62.52	35.80	1.69	0.668	1.768	26.944	10.180
g-C ₃ N ₄ (H ₂)	61.86	36.17	1.96	0.682	1.534	26.384	11.730

4.3.1.4 Electronic Band Structure of H-doped g-C₃N₄

The experimentally observed effects of nitrogen vacancy (V_N) and hydrogen occupation at the nitrogen vacancy site (H_N) in $g-C_3N_4$ structures were studied by DFT based electronic structure calculations. Although the synthesized samples are terminated with NH_2 , the experimental structure of the lattice of tri-s-triazine is not known precisely due to its hydrogen bonding. Thus modeling defects in such structure is difficult. Further, the unit cell of tri-s-triazine could contain large number of atoms (196), which make the impurity modeling and electronic structure calculations computationally expensive. Therefore, for the modeling purpose $g-C_3N_4$ is taken into consideration as shown in Figure 4.8a.

Figure 4.8b shows the total and partial density of states (DOS) of the pristine $g-C_3N_4$, $g-C_3N_4$ with a two-coordinated N vacancy [$g-C_3N_4 (V_N)$] and $g-C_3N_4$ with H at N site [$g-C_3N_4 (H_N)$]. A band gap value of 1.34 eV was obtained for pristine $g-C_3N_4$ structure. Although underestimated as compared to the experimental value, this is comparable to the other results reported using GGA-PBE¹⁹⁰. We carried out band structure calculation of $g-C_3N_4$ by PBE0 hybrid functional to correct the band gap problem. However, the band gap value obtained by PBE0 is severely overestimated (4.2 eV), thus the calculations were done using GGA-PBE functional. To match the experimental band gap values, we have applied a scissor operator of 1.41 eV.

DOS analysis shows that nitrogen vacancy and hydrogen at nitrogen site induce mid gap states which results in band gap narrowing of 0.8 and 1.3 eV respectively. Thus for V_N and H_N the effective band gap was found to be 2.0 and 1.7 eV respectively. It is further noted that nitrogen vacancy results in pushing the effective valence band (VB) energy to more negative values while hydrogen at nitrogen site lowers the conduction

band (CB) energy to more positive values. Figure 4.8c and 4.8d show the site decomposed DOS analysis of perfect and defect g-C₃N₄ systems. In the case of nitrogen vacancy the extra states are mainly contributed by C 2p orbitals which could be attributed to the dangling bonds of carbon at the nitrogen vacant site. In the case of H at N site, it is worth noting that H induced states do not appear in the band gap. H 1s peaks appear in the VB region located at around -6 eV to -2 eV. These energy states overlap with the energy states of C p, indicating a bonding takes place with C-H. The extra energy states in the mid-gap are contributed by C 2p and N 2p orbitals. The impurity induced states are not localized on H atoms. In contrary to the common electronic structure produced by the defects, this case is different. Many examples are present such as N S, F, Cu doping in oxides where defect localized states occur^{59, 61, 195, 196}. In impurity localized states, separation of electron is difficult. Further, the impurity may act recombination centre. However in this case, the photoexcited electrons are not localized and are easy to separate.

When nitrogen vacancy was created in g-C₃N₄ lattice, the change in the total energy was 1.32 eV (per formula unit) while for H at N site the change in total energy was 0.78 eV (per formula unit). These values clearly indicate that H occupation at N site is thermodynamically favored. As samples were grown in hydrogen atmosphere, the formation energy of H doping at nitrogen would further be reduced and thus H doping at N site would occur. The electronic structure calculations agree well with the observed band gap reduction and thus it is further confirmed that H at N site in g-C₃N₄ is responsible for inducing visible light absorption.

Figure 4.8 a) Unit cell of g-C₃N₄. b) Total and partial density of states of (i) pristine g-C₃N₄, (ii) g-C₃N₄ with two-coordinated N vacancy, (iii) g-C₃N₄ with H atom at two-coordinated N vacancy site. c) Site decomposed DOS on (i) C in N vacancy and (ii) N in N vacancy. d) Site decomposed DOS on (i) C in H substituted at N site, (ii) N in H substituted at N site, (iii) H in H substituted at N site. Color code: red (s), blue (p) and black (total).

Figure 4.9 shows the band alignment of the individual photocatalysts with respect to the $\text{H}_2/\text{H}_2\text{O}$ reduction potential. It is known that the conduction band potentials of rutile, anatase and brookite are in the increasing reducing ability of protons respectively. The pristine $\text{g-C}_3\text{N}_4$ has conduction band potential at 1.12 eV wrt $\text{H}_2/\text{H}_2\text{O}$ reduction level and it is around -0.55 eV more negative to the energy of brookite TiO_2 phase. DFT calculations predict that defect structures of C_3N_4 , alter its band edge potentials significantly. As seen from PDOS plots, nitrogen vacancy pushes the valence band to more negative values, thus the oxidation potential of the band is lowered for water splitting reaction. For hydrogen substitution at nitrogen site, the conduction band potential is lowered to positive values while valence band potential is lowered to negative values.

Figure 4.9 Band diagram of $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4 (\text{V})_{\text{N}}$, $\text{g-C}_3\text{N}_4 (\text{H})_{\text{N}}$, brookite, anatase and rutile TiO_2 relative to redox potential of water at pH 7^{21, 35, 124, 125, 177}.

In short, from all the evidences provided, it is confirmed that with the introduction of forming gas or H_2 gas in the synthesis process, N vacancies are formed which will leave the neighboring C atoms with unbonded electrons. H atom could occupy the N vacancy site, reacts with the C atom unbonded electron and form C-H bond. As reported, with N vacancies in $g-C_3N_4$, additional electrons states are formed above the valence band ¹⁹² and thus resulting in the red-shift of the absorption edge and the enhancement of absorption in the visible light region. In similar cases, researchers reported visible light active black TiO_2 with heat treatment of rutile TiO_2 in H_2 gas to form oxygen vacancies and localized states in the band gap ¹⁹⁷⁻¹⁹⁹.

4.3.1.5 Morphology, Topography and Surface Area of H-doped $g-C_3N_4$

The morphology of the $g-C_3N_4$ (air), $g-C_3N_4$ (N_2), $g-C_3N_4$ (forming) and $g-C_3N_4$ (H_2) samples were shown in Figure 4.10. From the FESEM images, all samples have sheet structures and are highly agglomerated. From the TEM images, the $g-C_3N_4$ (forming) sheets are observed to be folded which results in rolled edges whereas for the $g-C_3N_4$ (H_2) sample, it has flat sheet structure with well-distributed pores of 40-50 nm. Table 4.2 shows the BET surface areas of the $g-C_3N_4$ (air), $g-C_3N_4$ (N_2), $g-C_3N_4$ (forming) and $g-C_3N_4$ (H_2) samples. The surface area of $g-C_3N_4$ (H_2) is 3 times that of $g-C_3N_4$ (air), which could be due to the pore structure of $g-C_3N_4$ (H_2). The thickness of $g-C_3N_4$ (air) and $g-C_3N_4$ (H_2) sheets were determined by measuring the height difference between two layers from topographic images obtained by AFM as shown in Figure 4.11. Due to the equipment limitation to measure such thin thickness in nanometer size, many random

areas were measured and the most prominent range of thickness with the highest occurrence was chosen. From Figure 4.11c and 4.11d, it can be estimated that g-C₃N₄ (air) and g-C₃N₄ (H₂) sheets have thickness of approximately 3.01 to 3.5 nm and 2.01 to 3 nm respectively, indicating 9 to 11 layers and 6 to 9 layers of g-C₃N₄ respectively. Based on BET surface area analysis, the surface area of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂) samples increases from 5.87, 6.73, 9.41 to 20.91 m² g⁻¹ respectively with g-C₃N₄ (H₂) having the highest surface area which could be due to the porous structure as observed from the TEM image. Moreover, the N₂ adsorption and desorption isotherm as shown in Figure 4.12a confirms the mesoporous structure with type I hysteresis loop being observed for the g-C₃N₄ (forming) and g-C₃N₄ (H₂) samples. From the pore size distribution obtained from its absorption isotherm as shown in Figure 4.12b, the average pore size of g-C₃N₄ (H₂) is about 40 nm which is consistent with the pore size observed from the TEM image. Hence, with the introduction of H₂ in the process of polycondensation, it results in different chemical structure, electronic structure, optical properties, surface area and porosity which will affect the photocatalytic activity.

Figure 4.10 FESEM images of a) g-C₃N₄ (air), b) g-C₃N₄ (N₂), c) g-C₃N₄ (forming) and d) g-C₃N₄ (H₂). TEM images of e) g-C₃N₄ (forming) and f) g-C₃N₄ (H₂).

Table 4.2 Surface areas of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂).

Sample	BET Surface Area (m ² g ⁻¹)
g-C ₃ N ₄ (air)	5.87
g-C ₃ N ₄ (N ₂)	6.73
g-C ₃ N ₄ (forming)	9.41
g-C ₃ N ₄ (H ₂)	20.91

Figure 4.11 Tapping-mode AFM images of a) g-C₃N₄ (air) and b) g-C₃N₄ (H₂). Range of thickness of c) g-C₃N₄ (air) and d) g-C₃N₄ (H₂) determined by measuring many random areas of difference of vertical distance between two layers.

Figure 4.12 a) Adsorption and desorption isotherms of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂). b) Pore size distribution of g-C₃N₄ (H₂).

4.3.1.6 Visible Light-Driven Hydrogen Production via Photocatalytic Water Splitting with H-doped g-C₃N₄

The photocatalytic activities of g-C₃N₄ (air), g-C₃N₄ (N₂), g-C₃N₄ (forming) and g-C₃N₄ (H₂) samples were appraised via the photocatalytic hydrogen production under visible light irradiation as shown in Figure 4.13. In comparison with g-C₃N₄ (air) and g-C₃N₄ (N₂) samples, both g-C₃N₄ (forming) and g-C₃N₄ (H₂) samples show higher H₂ production with g-C₃N₄ (H₂) producing the highest amount of H₂ with 4.8 times the amount of H₂ produced with g-C₃N₄ (air). The improved photocatalytic activity of g-C₃N₄ (H₂) can be explained with the increased optical absorption in the visible range, higher surface area and open pore structure which is beneficial for mass transfer. However, even though there is improvement in H₂ production with g-C₃N₄ (forming) and g-C₃N₄ (H₂) as

compared to $\text{g-C}_3\text{N}_4$ (air) and $\text{g-C}_3\text{N}_4$ (N_2), the amount of H_2 produced is still insufficient. Thus, to further enhance the H_2 production, the fast photogenerated electron-hole recombination should be reduced by forming a heterojunction where charge carriers could be transferred from one material to another leading to charge separation. As such, $\text{g-C}_3\text{N}_4$ (forming) or $\text{g-C}_3\text{N}_4$ (H_2) was mixed and heat treated with two-phase anatase/brookite TiO_2 to create heterojunction to further enhance the photocatalytic activities. A two-phase anatase/brookite TiO_2 was used instead of a single phase TiO_2 for more effective charge separation which will be proven in the next section.

Figure 4.13 Hydrogen evolved per gram of catalyst under visible light irradiation with 420 nm cut off filter in aqueous triethanolamine solution (20 vol%) over 1 wt% Pt loaded photocatalysts; $\text{g-C}_3\text{N}_4$ (air), $\text{g-C}_3\text{N}_4$ (N_2), $\text{g-C}_3\text{N}_4$ (forming) and $\text{g-C}_3\text{N}_4$ (H_2).

4.3.2 H-doped g-C₃N₄ with two-phase anatase/brookite TiO₂

4.3.2.1 Crystal Structure of H-doped g-C₃N₄ with Two-Phase Anatase/Brookite TiO₂

Different amount of g-C₃N₄ (forming) was mixed with two-phase anatase/brookite TiO₂ as such: 20 wt% of g-C₃N₄ (forming) with 80 wt% of two-phase anatase/brookite TiO₂ (**20CN(f)-80AB**), 50 wt% of g-C₃N₄ (forming) with 50 wt% of two-phase anatase/brookite TiO₂ (**50CN(f)-50AB**), 80 wt% of g-C₃N₄ (forming) with 20 wt% of two-phase anatase/brookite TiO₂ (**80CN(f)-20AB**) and 90 wt% of g-C₃N₄ (forming) with 10 wt% of two-phase anatase/brookite TiO₂ (**90CN(f)-10AB**). After ball milling and heat treatment with two-phase anatase/brookite TiO₂, the crystal structure of g-C₃N₄ remains unchanged with two distinctive peaks of the (100) and (002) planes as shown in Figure 4.14. With higher amount of g-C₃N₄ in the mixture, the intensity of the (002) plane of g-C₃N₄ increases with respect to the TiO₂ peak. However, there is a shift of the (002) peak from 27.4 ° to 27.7 ° for 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB and to 27.8 ° for 90CN(f)-10AB sample indicating a decreased interplanar spacing between the layers of g-C₃N₄ sheets and a denser stacking. Niu et al. reported improved photocatalytic activity of g-C₃N₄ nanosheets by heating the bulk g-C₃N₄ in air at 500 °C for 2 hours which leads to thermal oxidation etching resulting in decreased layers of sheets and denser stacking with lower interplanar spacing between the sheets¹⁸².

Figure 4.14 XRD patterns of g- C_3N_4 (forming)/anatase/brookite TiO_2 mixtures; 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB and 90CN(f)-10AB.

4.3.2.2 Morphology, Surface Area and Optical Properties of H-doped g- C_3N_4 with Two-Phase Anatase/Brookite TiO_2

Furthermore, from the FESEM image in Figure 4.15a, less agglomeration of the sheets is observed and the TEM image in Figure 4.15b shows thinner g- C_3N_4 sheets with nanosheets structure. The nanoparticles and plates observed in TEM image are anatase and brookite TiO_2 as discussed in Chapter 2. Thus, by heating the g- C_3N_4 /anatase/brookite TiO_2 mixture, it not only enhances the interfacial contact between g- C_3N_4 and anatase/brookite TiO_2 , but also results in more densely packed nanosheets structure in g- C_3N_4 .

Figure 4.15 a) FESEM and b) TEM images of 80CN(f)-20AB.

In addition, with the increasing amount of $\text{g-C}_3\text{N}_4$ in the $\text{g-C}_3\text{N}_4/\text{anatase/brookite TiO}_2$ mixture, the surface area increases as shown in Table 4.3. The surface area of $\text{g-C}_3\text{N}_4$ (forming) and two-phase anatase/brookite TiO_2 before heat treatment are 9.67 and $23.77 \text{ m}^2 \text{ g}^{-1}$ and after heat treatment, both 80CN(f)-20AB and 90CN(f)-10AB have surface area of 33.61 and $56.40 \text{ m}^2 \text{ g}^{-1}$ respectively which are higher than surface area of two-phase anatase/brookite TiO_2 before heat treatment. The surface area of titania nanostructures are

reported to decrease after heat treatment ¹⁶². However, in our case, there is an increase of surface area after heat treatment and the surface area increases with amount of g-C₃N₄. Thus, this shows that the g-C₃N₄ underwent structural change during heat treatment which results in higher surface area. As such, it provides additional evidence that during heat treatment, thermal oxidation etching occurs resulting in nanosheets structure with decreased layers of sheets and higher surface area. Moreover, from the N₂ adsorption and desorption isotherm as shown in Figure 4.16, the pore size of the mesoporous structure of g-C₃N₄ decreases with increasing amount of g-C₃N₄ in the g-C₃N₄/anatase/brookite TiO₂ mixture which could result in higher surface area.

Table 4.3 Surface area of the g-C₃N₄ (forming)/anatase/brookite TiO₂ mixtures, g-C₃N₄ (forming) and two-phase anatase/brookite TiO₂.

Sample	BET Surface Area (m ² g ⁻¹)
20CN(f)-80AB	18.59
50CN(f)-50AB	18.53
80CN(f)-20AB	33.61
90CN(f)-10AB	56.40
g-C ₃ N ₄ (forming)	9.67
anatase/brookite TiO ₂	23.77

Figure 4.16 Adsorption and desorption isotherms of g-C₃N₄ (forming)/anatase/brookite TiO₂ mixtures; 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB and 90CN(f)-10AB.

Figure 4.17 shows the UV-Vis diffuse reflectance spectra for g-C₃N₄/anatase/brookite TiO₂ mixture, two-phase anatase/brookite TiO₂ and g-C₃N₄ (forming). For two-phase anatase/brookite TiO₂, it has absorption edge at 385 nm as the band gap of anatase and brookite are 3.2 eV and 3.3 eV respectively^{90, 125}. With increasing amount of g-C₃N₄ in the g-C₃N₄/anatase/brookite TiO₂ mixture, the optical absorption extends to longer wavelength in the visible light region due to the visible light absorption of g-C₃N₄.

Figure 4.17 UV-Vis diffuse reflectance spectra of $\text{g-C}_3\text{N}_4$ (forming), two-phase anatase/brookite TiO_2 denote A-B TiO_2 and $\text{g-C}_3\text{N}_4$ (forming)/anatase/brookite TiO_2 mixtures; 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB, 90CN(f)-10AB.

4.3.2.3 Visible Light-Driven Hydrogen Production via Photocatalytic Water Splitting and Photoluminescence with H-doped $\text{g-C}_3\text{N}_4$ with Two-Phase Anatase/Brookite TiO_2

The photocatalytic H_2 production under visible light irradiation with $\text{g-C}_3\text{N}_4$ (forming)/anatase/brookite TiO_2 mixtures with different weight ratio of two-phase anatase/brookite TiO_2 and $\text{g-C}_3\text{N}_4$ (forming) are shown in Figure 4.18a. The photocatalytic H_2 production with pure $\text{g-C}_3\text{N}_4$ (forming) sample is included in Figure 4.18a as well for comparison and to show the effect of the addition of TiO_2 with $\text{g-C}_3\text{N}_4$ (forming). From Figure 4.18a, all $\text{g-C}_3\text{N}_4$ /anatase/brookite TiO_2 mixtures, 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB and 90CN(f)-10AB, produce higher amount of H_2

than pure g-C₃N₄ (forming). With increasing amount of g-C₃N₄ (forming) in the g-C₃N₄/anatase/brookite TiO₂ mixture, H₂ evolution increases with 80CN(f)-20AB producing the highest amount of H₂ which is 108 times the amount of H₂ produced with pure g-C₃N₄ (forming). This great enhancement could be attributed to the g-C₃N₄ nanosheets structure, higher surface area with mesoporous structure, enhanced optical absorption in the visible light region and more importantly the presence of the g-C₃N₄/TiO₂ heterojunction leading to effective charge separation resulting from the photo-generated electrons transfer from the more cathodic conduction band of g-C₃N₄ to the conduction band of brookite and anatase TiO₂. As mentioned, Niu et al. reported the improved photocatalytic activity of g-C₃N₄ nanosheets by heat treatment of bulk g-C₃N₄ in air for thermal oxidation etching to obtain nanosheets structure with decreased layers of sheets¹⁸². By further heat treating g-C₃N₄ (forming) in air at 450 °C, the H₂ production is higher than g-C₃N₄ (forming) without further heat treatment as shown in Figure 4.19 due to decreased layers of sheets and denser stacking with lower interplanar spacing between the sheets. However, without the addition of TiO₂ to form heterojunction, the enhancement of H₂ is not as great as with the addition of TiO₂ together with heat treatment. Thus, charge separation plays an important role in enhancing the photocatalytic activity.

With further increment of g-C₃N₄ in the mixture to 90 wt% of g-C₃N₄ (forming) and 10 wt% of anatase/brookite TiO₂ (90CN(f)-10AB), the H₂ production decreases but is still higher than pure g-C₃N₄ (forming) (see Table 4.4). This could be due to the low amount of TiO₂ present which is not sufficient for effective charge transfer from g-C₃N₄ to TiO₂ due to the fast photogenerated electron-hole recombination in the g-C₃N₄ of much higher

amount. PL analysis was performed to investigate the charge separation efficiency of the g-C₃N₄/anatase/brookite TiO₂ mixtures and pure g-C₃N₄ (forming) samples as shown in Figure 4.20a. The higher the PL intensity is, the more the recombination of the photogenerated electron-hole pair. From Figure 4.20a, pure g-C₃N₄ (forming) has the highest PL intensity followed by 90CN(f)-10AB, 20CN(f)-80AB, 50CN(f)-50AB and 80CN(f)-20AB has the lowest PL intensity. Hence, the lowest H₂ production with pure g-C₃N₄ (forming) is caused by the fast recombination of the electron-hole pairs and the lower H₂ production with 90CN(f)-10AB is attributed to the less effective charge separation while 80CN(f)-20AB having the highest H₂ production is attributed to the more effective charge separation. Hence, effective charge separation plays an important role in enhancing the H₂ production and the number and type of TiO₂ phases present will greatly affect the charge separation.

Pure anatase and brookite TiO₂ were synthesized, ball milled and heat treated with 80 wt% of g-C₃N₄ (forming) in the same condition as g-C₃N₄/anatase/brookite TiO₂ mixture. 80 wt% of g-C₃N₄ (forming) with 20 wt% of anatase TiO₂ is named as 80CN(f)-20A and 80 wt% of g-C₃N₄ (forming) with 20 wt% of brookite TiO₂ is named as 80CN(f)-20B. The H₂ production of these samples was compared and is shown in Figure 4.18b. With the addition of single phase anatase or brookite TiO₂, the H₂ production is higher than pure g-C₃N₄ (forming) (see Table 4.4). Again, this is due to the photogenerated electron transfer from the conduction band of g-C₃N₄ to the conduction of anatase or brookite phase as the conduction band potential of g-C₃N₄ is more cathodic than the conduction band potential of brookite and anatase TiO₂. In addition, 80CN(f)-20B produces more H₂ than 80CN(f)-20A which is attributed to the more cathodic conduction band potential of

the brookite phase than the anatase phase as shown in Figure 4.9. With a higher cathodic conduction band potential, it energetically favors proton reduction to form H_2 as brookite TiO_2 produces higher amount of H_2 than anatase TiO_2 . As a result, after the electrons are being transferred from the conduction band of g- C_3N_4 to the conduction band of brookite and anatase respectively, the electrons on the more cathodic conduction band of brookite will be more energetically favorable to reduce water to form hydrogen gas than the electrons on the conduction band of anatase. Hence, higher production of H_2 is achieved with 80CN(f)-20B than 80CN(f)-20A.

In comparison with the single TiO_2 mixture with g- C_3N_4 , two-phase anatase/brookite TiO_2 mixture with g- C_3N_4 produces higher amount of H_2 . This is attributed to more effective charge separation with the two-phase anatase/brookite TiO_2 than single phase TiO_2 as evidenced from the PL spectra in Figure 4.20b. 80CN(f)-20AB has the lowest PL intensity followed by 80CN(f)-20B, 80CN(f)-20A and g- C_3N_4 (forming) with the highest PL intensity. After the photo-generated electrons are transferred from g- C_3N_4 to brookite, some of the electrons on the brookite conduction band can reduce protons to form H_2 while some of the electrons can be further transferred from brookite to the anatase phase and reduce protons to form H_2 . As a result, it leads to more effective charge separation and higher H_2 production.

P25 is a well-known commercial TiO_2 of high photocatalytic activity with 75 wt% of anatase and 25 wt% of rutile. Similarly, P25 was ball milled and heated with 80 wt% of g- C_3N_4 (forming) and it is named as 80CN(f)-20P25. To have a mixture of g- C_3N_4 with three-phase TiO_2 , rutile TiO_2 was obtained by heat treating the two-phase anatase/brookite TiO_2 at a high temperature. Similarly, 80 wt% of g- C_3N_4 (forming), 15

wt% of two-phase anatase/brookite TiO_2 and 5 wt% of rutile TiO_2 (a total of 20 wt% of TiO_2) were ball milled and heat treated. This mixture is named as 80CN(f)-15AB-5R. From Figure 4.18b, even though two-phase TiO_2 is present in the 80CN(f)-20P25 with anatase and rutile TiO_2 , the H_2 generated is not as high as 80CN(f)-20AB and even lower than g- C_3N_4 with brookite TiO_2 (80CN(f)-20B). This is due to the less cathodic conduction band potential of the anatase and rutile phases as compared to brookite phase. In addition, the conduction band potential of rutile is less cathodic than the chemical potential for water reduction as shown in Figure 4.9. As a result, after the photogenerated electrons are being transferred onto the conduction band of rutile, it cannot reduce protons to form H_2 . Similarly, with three phase anatase/brookite/rutile TiO_2 in the mixture with g- C_3N_4 , the H_2 generated with 80CN(f)-15AB-5R is lower than the H_2 generated with 80CN(f)-20AB and 80CN(f)-20B due to the incapability of the electrons transferred on the rutile phase to reduce protons to produce H_2 . As such, the number and type of TiO_2 phase in the g- $\text{C}_3\text{N}_4/\text{TiO}_2$ mixture greatly affect the H_2 production and particularly, brookite phase play a big role in enhancing the photocatalytic activity in the g- $\text{C}_3\text{N}_4/\text{TiO}_2$ mixture. With the further addition of anatase phase to promote charge separation, two-phase anatase/brookite TiO_2 with g- C_3N_4 (forming) mixture produces the highest amount of H_2 .

Similarly, g- C_3N_4 (H_2) which produces more H_2 than g- C_3N_4 (forming) was ball milled and heat treated with 50 wt% of two-phase anatase/brookite TiO_2 and 20 wt% of two-phase anatase/brookite TiO_2 which are named as 50CN(H_2)-50AB and 80CN(H_2)-20AB respectively. 80 wt% of g- C_3N_4 (air) with 20 wt% of two-phase anatase/brookite TiO_2 is named as 80CN(air)-20A. The photocatalytic H_2 production under visible light irradiation

with 50CN(H₂)-50AB and 80CN(H₂)-20AB were shown in Figure 4.18c. The H₂ production with pure g-C₃N₄ (H₂), 80CN(air)-20AB and 80CN(f)-20AB were included in Figure 4.18c for comparison. Similarly, with the addition of two-phase anatase/brookite TiO₂ in the g-C₃N₄ (H₂) mixture, both 50CN(H₂)-50AB and 80CN(H₂)-20AB generate H₂ than pure g-C₃N₄ (H₂) due to the charge transfer from g-C₃N₄ (H₂) to TiO₂ resulting in effective charge separation. Comparing g-C₃N₄ (H₂)/TiO₂ mixture with g-C₃N₄ (air)/TiO₂ mixture, 80CN(H₂)-20AB produces 63 times of H₂ being produced from 80CN(air)-20AB. It is proposed that the rate of electron transfer across heterojunction strongly depends on the band off set of the semiconductors in contact with each other. Smaller band offsets result in faster electron transfer processes ¹⁶⁸. In the present case, the conduction band minimum offset between perfect g-C₃N₄ and brookite TiO₂ is around 0.55 eV while the band offset between H-doped g-C₃N₄ and brookite TiO₂ is around 0.07 eV as shown in Figure 4.9. The newly formed energy states in H-doped g-C₃N₄ could have a more favorable overlap with the conduction band of brookite phase and thus enabling faster transfer of electrons which lead to enhanced charge separation as evidenced from the PL analysis in Figure 4.20c. The PL intensity is the lowest with 80CN(H₂)-20AB, followed by 80CN(f)-20AB and 80CN(air)-20AB with the highest PL intensity which indicates the enhanced charge separation in the 80CN(H₂)-20AB sample. As a result, H₂ evolution is greatly enhanced with g-C₃N₄ (H₂)/two-phase anatase/brookite TiO₂ mixture than g-C₃N₄ (air)/two-phase anatase/brookite TiO₂ mixture due to the enhanced charge transfer. Figure 4.21 shows the schematic diagram of the electron transfer from H-doped g-C₃N₄ to brookite and anatase TiO₂ under visible light illumination.

Comparing g-C₃N₄ (H₂)/TiO₂ mixture with g-C₃N₄ (forming)/TiO₂ mixture as shown in Figure 4.18c, 80CN(H₂)-20AB generates higher amount of H₂ than 80CN(forming)-20AB as g-C₃N₄ (H₂) produces more H₂ than g-C₃N₄ (forming). Optimally, 80CN(H₂)-20AB produces the highest amount of H₂ and is stable over long period of time as shown in Figure 4.22. The stability of 80CN(H₂)-20AB was investigated for running 3 cycles of photoreaction over a total of 36 hours. After each cycle of 12 hours, the system was completely evacuated to remove the H₂ produced. After each run, the H₂ production did not degrade but increased. As the rate of H₂ production is consistent in each run, the increment of H₂ production in the run 2 and 3 is not due to any residual H₂ left in the system from run 1. Hence, by adding 20 wt% of two-phase anatase/brookite TiO₂ with 80 wt% of g-C₃N₄ (H₂) and heat treating the mixture, the H₂ production is the highest which is 363 times the amount of H₂ produced with g-C₃N₄ (air) and the mixture is photochemically stable over a long period of time.

Figure 4.18 Hydrogen evolved per gram of catalyst under visible light irradiation with 420 nm cut off filter in aqueous triethanolamine solution (20 vol%) over 1 wt% Pt loaded photocatalysts; a) g-C₃N₄ (forming) and g-C₃N₄ (forming)/anatase/brookite TiO₂ mixtures; 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB, 90CN(f)-10AB. b) g-C₃N₄ (forming) and 80 wt% of C₃N₄ (forming) with anatase, brookite, two-phase anatase/brookite TiO₂, P25 and rutile/anatase/brookite TiO₂ respectively. c) g-C₃N₄ (H₂), g-C₃N₄ (H₂)/anatase/brookite TiO₂ mixtures, 80CN(f)-20AB and 80CN(air)-20AB.

Figure 4.19 Hydrogen evolved per gram of catalyst under visible light irradiation with 420 nm cut off filter in aqueous triethanolamine solution (20 vol%) over 1 wt% Pt loaded photocatalysts; g-C₃N₄ (forming), g-C₃N₄ (forming) with heat treatment at 450 °C for 2 hours without TiO₂ (denoted as g-C₃N₄ (forming)-HT450) and 20CN(f)-80AB.

Table 4.4 Hydrogen evolved ($\mu\text{mol g}^{-1}$) under visible light irradiation in aqueous triethanolamine solution over 1 wt% Pt loaded photocatalysts with 12 hours of reaction.

Sample	Total H ₂ produced at the 12 th hour ($\mu\text{mol g}^{-1}$)
g-C ₃ N ₄ (air)	1.22
g-C ₃ N ₄ (N ₂)	1.67
g-C ₃ N ₄ (forming)	3.33
g-C ₃ N ₄ (H ₂)	5.88
20CN(f)-80AB	52.34
50CN(f)-50AB	69.02
80CN(f)-20AB	359.64
90CN(f)-10AB	4.65
80CN(f)-20A	8.10
80CN(f)-20B	130.06
80CN(f)-P25	64.37
80CN(f)-15AB-5R	82.72
50CN(H ₂)-50AB	80.16
80CN(H ₂)-20AB	442.9
80CN(air)-20AB	7.02

Figure 4.20 a) PL spectra of g-C₃N₄ (forming) and g-C₃N₄ (forming)/anatase/brookite TiO₂ mixtures; 20CN(f)-80AB, 50CN(f)-50AB, 80CN(f)-20AB, 90CN(f)-10AB. b) PL spectra of g-C₃N₄ (forming) and 80 wt% of g-C₃N₄ (forming) with anatase, brookite and two-phase anatase/brookite TiO₂ respectively. c) PL spectra of 80 wt% of g-C₃N₄ (air, forming or H₂) with 20 wt% of two-phase anatase/brookite TiO₂.

Figure 4.21 Schematic diagram of the electron transfer from H-doped g-C₃N₄ to two-phase anatase/brookite TiO₂ under visible light illumination.

Figure 4.22 Stability test for 80CN(H₂)-20AB in 3 continuous runs with evacuation at every 12 hours.

4.4 Conclusions for the Chapter

In conclusions, with the introduction of H₂ gas during the g-C₃N₄ polycondensation reaction, nitrogen vacancies and hydrogen substitution at nitrogen vacancy occur in the resulting material. As a result, there is an enhancement of solar absorption due to narrowing of g-C₃N₄ band gap energy. The synergistic effects of increased optical absorption in the visible range, higher surface area and open pore structure lead to higher photocatalytic activity of the g-C₃N₄. To further enhance the photocatalytic activity, g-C₃N₄ (forming) or g-C₃N₄ (H₂) was ball milled and heat treated with two-phase anatase/brookite TiO₂ to reduce the fast electron-hole recombination via effective charge transfer. The number and type of TiO₂ phase in the g-C₃N₄/TiO₂ mixture greatly affect

the H_2 production and with two-phase anatase/brookite TiO_2 , the H_2 evolution is the highest as compared to $\text{g-C}_3\text{N}_4$ with single phase anatase, brookite, two-phase anatase/rutile and three-phase anatase/brookite/rutile. With 20 wt% of two-phase anatase/brookite TiO_2 and 80 wt% of $\text{g-C}_3\text{N}_4$ (H_2), the H_2 production is the highest which is 363 times the amount of H_2 produced with $\text{g-C}_3\text{N}_4$ (air). The series of comparison further confirms the importance of charge separation in photocatalytic activity. It also reveals the importance of maintaining the conduction band potential position of all the constituent phases above the hydrogen reduction potential in order to maximize the full benefit of charge separation.

Chapter 5: Conclusions and Recommendations

In this thesis, to counter the challenges of fast electron-hole recombination and low solar to hydrogen conversion efficiency in the generation of solar hydrogen via photocatalytic water splitting, rational engineering has been developed to enhance the hydrogen production by enhancing the water reduction reaction with materials with more cathodic conduction band potential, improving the charge separation and increasing the solar absorption. Using various experimental and characterization techniques, the crystal structure, morphology, chemical structure, electronic band structure, surface area and optical properties of the photocatalyst have been studied in order to understand their effect on the solar hydrogen production.

The mains findings and contributions are as follows:

1. Synergistic Two-phase Anatase/Brookite TiO_2 Nanostructures for Enhanced Photocatalytic Hydrogen Production: A facile hydrothermal method which is able to control the phase and composition of anatase and brookite TiO_2 was developed using TiS_2 as the precursors. By varying the NaOH concentration, the ratio of anatase to brookite phase can be easily tailored. With the study on TiO_2 phases formed at different growth times at a fixed NaOH concentration, it was found out that sodium titanate was first formed at short growth time followed by sodium titanate with anatase and/or brookite mixture and subsequently anatase and/or brookite TiO_2 at longer growth time. With Rietveld refinement, the composition of anatase and brookite were found to remain unchanged even with longer growth time. Thus, this proved that anatase and brookite are

formed from the transformation of sodium titanate. With more cathodic conduction band potential of the brookite phase than anatase phase, the water reduction reaction to form hydrogen gas is energetically more favorable which results in higher hydrogen production. To further enhance the hydrogen production, two-phase anatase/brookite TiO_2 was synthesized to create a heterojunction for effective charge separation to inhibit the fast electron-hole recombination.

2. Further Enhancement of Photocatalytic H_2 Production with Reduced Graphene Oxide-Anatase/Brookite TiO_2 Mixtures: To further counter the fast electron-hole recombination, rGO was coupled with two-phase anatase/brookite TiO_2 via chemical reduction of GO. To date, there is no report on coupling rGO with two-phase anatase/brookite TiO_2 where most of rGO- TiO_2 composites reported are anatase, rutile or anatase/rutile TiO_2 with rGO. By coupling rGO with two-phase anatase/brookite TiO_2 , the hydrogen production was greatly enhanced as compared to two-phase anatase/brookite TiO_2 without rGO due to the improved charge separation as evidenced by PL spectroscopy and the higher surface area. In addition, the hydrogen production is higher with rGO-anatase/brookite TiO_2 than rGO-P25 (anatase/rutile) due to the higher reduction power to reduce water with rGO-anatase/brookite TiO_2 mixture.

3. Enhanced Visible Light Hydrogen Production with Hydrogenated $\text{g-C}_3\text{N}_4$ on Two-phase Anatase/Brookite TiO_2 Heterostructure: A novel approach to tune the photophysical properties of $\text{g-C}_3\text{N}_4$ for efficient photocatalytic hydrogen production was developed by introducing hydrogen gas in the polycondensation reaction of $\text{g-C}_3\text{N}_4$ to create N vacancy and H substitution at N vacancy. With various characterization techniques and simulation analysis, nitrogen vacancy and H substitution at N vacancy are

proven to be formed in g-C₃N₄ (H₂) which causes the narrowing of the band gap to 2.0 eV while conventional g-C₃N₄ has band gap of 2.7 eV. With increased optical absorption in the visible range, higher surface area and open pore structure, the photocatalytic hydrogen production under visible light illumination is enhanced as compared to g-C₃N₄ synthesized from the conventional method. To further improve the hydrogen production by countering the fast electron-hole recombination, the H-doped g-C₃N₄ was coupled with two-phase anatase/brookite TiO₂ for effective charge separation. Although the enhancement of hydrogen production with g-C₃N₄/TiO₂ mixture was reported, the TiO₂ used in these reports was a single phase anatase TiO₂ or anatase/rutile. Results have shown that the number and type of TiO₂ phase in the g-C₃N₄/TiO₂ mixture greatly affect the hydrogen production. When H-doped g-C₃N₄ was coupled with two-phase anatase/brookite TiO₂, the hydrogen evolution is the highest as compared to H-doped g-C₃N₄ with single phase anatase, brookite, two-phase anatase/rutile and three-phase anatase/brookite/rutile. In addition, the hydrogen evolution is greatly enhanced with g-C₃N₄ (H₂)/TiO₂ mixture than g-C₃N₄ (air)/TiO₂ mixture due to the improved charge transfer with lower conduction band offset between H-doped g-C₃N₄ and brookite TiO₂. Thus, both H-doped g-C₃N₄ and two-phase anatase/brookite TiO₂ play an important role in enhancing the photocatalytic hydrogen production.

A summary of work in this thesis is summarized in the flow chart in Figure 5.1.

Figure 5.1 Flowing chart showing a summary of work done in this study.

Recommendations for Future Work

One of the most ideal routes to produce hydrogen using solar energy is the direct overall water splitting with the use of both photogenerated electrons and holes to reduce and oxidize water to produce hydrogen and oxygen gases simultaneously. Due to the fast electron-hole recombination, sacrificial agents are usually added in the water to enhance the photocatalytic hydrogen production. However, the consumption of the sacrificial agents is not a sustainable process, thus it would be desirable to develop a pure water

splitting system that is able to produce hydrogen efficiently without the use of sacrificial agent. To achieve this with the g-C₃N₄/TiO₂ mixture, hydrogen evolution co-catalyst such as Pt could be loaded on the g-C₃N₄ while oxygen evolution co-catalyst such as IrO₂ or RuO₂ could be loaded on TiO₂. As the conduction band potential of g-C₃N₄ is more negative than TiO₂, g-C₃N₄ would be a better hydrogen evolution photocatalyst (HER) than TiO₂ while the valence band potential of TiO₂ is more positive than g-C₃N₄, TiO₂ would be a better oxygen evolution photocatalyst (OER) than g-C₃N₄ (Figure 4.9). By loading IrO₂ or RuO₂ co-catalyst on TiO₂, the photogenerated holes in TiO₂ would be transferred to the co-catalyst and oxidize water to form oxygen gas and protons resulting in effective charge separation. On the other hand, by loading Pt co-catalyst on g-C₃N₄, the photogenerated electrons in g-C₃N₄ would be transferred to Pt and reduce the adsorbed protons to form hydrogen gas which similarly results in effective charge separation.

To further improve the charge separation, Z-scheme system could be employed with the use of an electron mediator such as rGO to accept electrons from OER and holes from HER. Although Fe³⁺/Fe²⁺ or IO₃⁻/I⁻ is commonly used as the electron mediators to shuttle electrons from OER to HER, a solid electron mediator is more favorable in the recovery of the photocatalyst and reclamation of clean water²⁰⁰. Iwase et al. reported the use of rGO as a solid electron mediator or electron conductor which help to transfer the electrons from BiVO₄ (OER) to the holes in Ru/SrTiO₃:Rh (HER) resulting in 3 times enhancement of gas evolution. This mechanism of electron flow improved the charge separation efficiency in each photocatalyst, leaving electrons in Ru/SrTiO₃:Rh and holes in BiVO₄ to split the water²⁰⁰. Thus, we proposed to use rGO as the electron mediator

with Pt loaded g-C₃N₄ as HER and IrO₂ or RuO₂ loaded TiO₂ as OER in direct overall water splitting to further enhance the oxygen and hydrogen evolution. The proposed schematic mechanism is shown in Figure 5.3 where photogenerated electrons from TiO₂ are transferred to rGO to recombine with the holes from g-C₃N₄. This leaves electrons in g-C₃N₄ and holes in TiO₂ to split the water more effectively.

Figure 5.2 Z-scheme photocatalysis system consisting of Ru/SrTiO₃:Rh (HER), BiVO₄ (OER) and photoreduced rGO (electron mediator) under visible-light irradiation²⁰⁰.

Figure 5.3 Proposed schematic mechanism of pure water splitting in a Z-scheme photocatalysis system consisting of Pt loaded $\text{g-C}_3\text{N}_4$ (HER) and IrO_2 or RuO_2 loaded TiO_2 (OER) under solar light irradiation.

List of Publications

Journal Publications

1. **Q. L. Tay**, X. F. Liu, Y. X. Tang, Z. L. Jiang, T. C. Sum, Z. Chen “Enhanced Photocatalytic Hydrogen Production with Synergistic Two-Phase Anatase/Brookite TiO₂ Nanostructures”, The Journal of Physical Chemistry C, 2013, 117, 14973-14982
2. **Q. L. Tay**, Z. Chen “Effective Charge Separation towards Enhanced Photocatalytic Activity via Compositing Reduced Graphene Oxide with Two-phase Anatase/Brookite TiO₂” (to be submitted)
3. **Q. L. Tay**, P. Kanhere, C. F. Ng, S. Chen, X. H. Wang, J. D. Hong, S. Chakraborty, A. C. H. Huan, T. C. Sum, Q. Zhang, R. Xu, R. Ahuja, Z. Chen “Defect Engineered g-C₃N₄ for Efficient Visible Light Hydrogen Production” (To be submitted)
4. **Q. L. Tay**, P. Kanhere, X. H. Wang, Q. Zhang, Z. Chen “Enhanced Visible Light Hydrogen Production with g-C₃N₄/Anatase-Brookite TiO₂ Heterojunction Structure” (To be submitted)

Conference Presentations

Oral Presentation:

1. “Photocatalytic water splitting using two-phase anatase/brookite TiO_2 nanoparticles” 244th ACS National Meeting, Aug 2012, Philadelphia, The United States of America

Poster Presentations:

1. “Photocatalytic Water Splitting with Synergistic Two-Phase Anatase/Brookite TiO_2 Nanostructures” 2013 MRS Fall Meeting, Nov 2013, Boston, The United States of America
2. “Enhanced Visible Light Hydrogen Production with g- C_3N_4 on A Two-phase TiO_2 Heterostructure” 3rd International Workshop on Natural and Artificial Photosynthesis, June 2014, Singapore

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