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HIERARCHICALLY STRUCTURED TiO_2 NANOROD SPHERES FOR CLEAN WATER AND ENERGY PRODUCTION

BAI HONGWEI

School of Civil and Environmental Engineering

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BAI HONGWEI

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SUMMARY

This study focuses on the synthesis of hierarchical TiO₂ nanorod spheres for photocatalytic water purification and clean energy generation. These hierarchical TiO₂ nanorod spheres were firstly synthesized from a facile low-temperature template-free hydrothermal method. In this novel approach, NaCl supersaturated TiCl₃ solution was used as the precursor. The presence of an acidic environment induces the outward growth of rutile TiO₂ along the [001] direction due to the adsorption of Cl⁻ on the (110) plane of rutile TiO₂ irrevocably leading to the formation of hierarchical TiO₂ nanorod spheres. Subsequently, hierarchical TiO₂ nanorod spheres were uniformly assembled on a piece of commercial membrane forming a novel hierarchical TiO₂ nanorod membrane suitable for concurrent photocatalysis and membrane filtration of wastewaters.

Experimental results demonstrated that the hierarchical TiO₂ nanorod membrane exhibited improved removal rates of humic acid (HA) and methylene blue (MB) compared to TiO₂ P25 (Degussa) deposited membrane due to the higher photocatalytic activity. Moreover, it exhibited higher permeate flux due to the porous functional layer created by hierarchical TiO₂ nanorod spheres which allows easy water pass through in a comparison to the dense layer formed by TiO₂ P25 nanoparticles. This demonstrates the ability of the hierarchical TiO₂ nanorod membrane to achieve photocatalytic water purification with no/less fouling, while simultaneously obtaining high water quality and high water production ability. Hence, with this approach the advantages of TiO₂ photocatalysis and membrane filtration can

be maximized by concurrently minimizing their disadvantages (membrane fouling and recovery of TiO_2).

Furthermore, well crystallized hierarchical TiO_2 nanorod spheres synthesized from hydrothermal methods were hard to reproduce at large scale. Therefore, we developed a facile high temperature calcination process to fabricate hierarchical TiO_2 nanorod spheres to overcome the drawbacks of hydrothermal method. Using a novel technique, an inorganic titanium precursor (TiCl_3) was added to a resorcinol (R) and formaldehyde (F) reaction solution under continuous heating and stirring for the preparation of crescent Ti/RF spheres. The presence of Cl^- stimulates the growth of rutile TiO_2 along the [001] direction. Additionally, the cross-linked RF spheres act as templates for TiO_2 nanorods in allowing the formation of crescent Ti/RF spheres through an *in-situ* wrapping up process. Thereafter, crescent Ti/RF spheres were calcined to remove the remaining organics and to promote crystallization of TiO_2 which allows the formation of monodisperse and well crystallized hierarchical TiO_2 nanorod spheres.

The hierarchical TiO_2 nanorod spheres synthesized from this approach demonstrated high photocatalytic activity for water purification and H_2 generation in a UV irradiated methanol/water sacrificial reagent system. In addition, it was found that despite calcinations at various temperatures the hierarchical TiO_2 nanorod spheres exhibited similar photocatalytic activities. However, it will be more cost effective to fabricate hierarchical TiO_2 nanorod spheres at an optimal temperature of 500 °C.

Moreover, by comparing the hierarchical TiO₂ nanorod spheres synthesized through hydrothermal and calcination method, we found that hierarchical TiO₂ nanorod spheres fabricated through calcinations enable scale up fabrication with better consistency and photocatalytic activity compared to that fabricated through hydrothermal method.

In summary, the adopted approach of scale up fabrication of hierarchical TiO₂ nanorod spheres through high temperature calcination has demonstrated great significance in the practical application of photocatalytic water purification and clean energy generation.

LIST OF PUBLICATIONS

Journals

1. **Bai, H. W.**, Z. Y. Liu and D. D. Sun (2013) “Single Crystalline Micro-/Nano- V_2O_5 Nanoflake Spheres as Cathode Materials for High-Energy and High-Power Lithium Ion-Batteries” *RSC Advances*, **Accepted**. (IF:2.562)
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CHAPTER 1 INTRODUCTION

1.1. Background

Water is recognized as a vital resource in order to ensure survivability of mankind and life on earth (Langenberg 2002). However, due to industrialization and urbanization it has led to the rising global issues resulting from inadequate access to clean and fresh water. Many of these of global issues associated to lack of clean and fresh water are well known: 1.2 billion people lack access to safe drinking water, 2.6 billion people have little or no sanitation, millions of people die annually – 3,900 children a day-from diseases transmitted through unsafe water of human excreta (Shannon et al. 2008, Elimelech and Phillip 2011).

Besides the issue of inadequate clean water, the 1st United Nation World Water Development Report – “Water for People, Water for Life” by the World Water Assessment Program has also mentioned (Programme 2003): *“The centrality of freshwater in our lives cannot be overestimated. Water has been a major factor in the rise and fall of civilizations. It has been a source of tensions and fierce competition between nations that could become even worse if present trends continue. Lack of access of water for meeting basic needs such as health, hygiene and food security undermines development and inflicts enormous hardship on more than a billion members of the human family. And its quality reveals everything, right or wrong, that we do in safeguarding the global environment.”*

In addition to the influence on the basic human demand, water also strongly affects energy and food production, industrial output, quality of environment, and global economy of both the developing and developed nations. Therefore, by temporally discarding global political debates pertaining to water resources and addressing water resource availability as a strategic component to national development; it will undoubtedly become an important and severely pressing issue to us in the next few decades. Moreover, in the recent years fresh water resources from rivers and lakes have been severely diminishing due to the increasing global population and rapid industrialization. Hence, the conflicts that arise due to the decline of water quality, water supply capacity and the exacerbation of water deteriorating situation are becoming more prominent and hard for reconciliation (Aldhous 2003a, b). This irreconcilable puzzle has caused scientists to devote to developing novel and alternative technologies for clean water production.

Coupled with the concern due to inadequate water resource, global energy issue is another challenge moving forward in the 21st century. Energy, is the driving force behind a nation's development and it guarantees the countries' competitive advantage, because it is the lifeblood of technological and economic development (Chow et al. 2003). However, the overdependence of global energy on fossil fuels has accelerated its depletion. Furthermore, the combustion of fossil fuels would also result in the emission of greenhouse gases which changes global climate at an unprecedented rate. Both these concerns have led to the world-wide attention on energy issues (Chow et al. 2003, Davis et al. 2010).

Facing these challenges scientists and researchers have been seeking for a novel and alternative technologies to produce clean energy and water. As such, membrane technology has been considered as a promising technology to produce clean water due to its special features such as high water quality and production rate. However, membrane fouling resulting from accumulation of particulates and organic substances in the pores or on the surface of membrane causes the rise of energy requirement and operational cost. Thus, membrane technology have been classified as an energy intensive technology and posing a major challenge due to the need to curb emissions of greenhouse gases (Bai et al. 2010).

Significant research has been carried out on photocatalytic oxidation with the use of titanium dioxide (TiO_2). TiO_2 have demonstrated its ability to produce clean water via purifying a heavily polluted water due to its strong degradation ability of refractory organic pollutants (Araña et al. 2002). A study by Bae and Ohno (2009) showed that by using a concurrent photocatalytic and membrane filtration system, TiO_2 photocatalytic oxidation was able to concurrently purify water and mitigate membrane fouling under the irradiation of UV light. However, the application of TiO_2 photocatalytic oxidation in water purification field is still limited by the relatively-low photocatalytic activity of TiO_2 . Therefore, this demonstrates the need to synthesize novel high efficiency TiO_2 catalysts for water purification.

In addition, many researchers have also been developing alternative means of renewable energies to substitute fossil fuels and curb climate change. These renewable energies include nuclear energy (Barnham et al. 2006, Butler 2004), photovoltaic energy, wind energy, ocean tidal energy, and H₂ energy (Grossmann et al. 2010). However, in view of these environmental issues and the increasing need for high clean energy density, it has led to the increasing recognition of H₂ energy as an alternative clean energy source (Kudo 2006, 2007, Liu et al. 2011a). H₂ energy is a proven and promising clean energy for these reasons (Liu et al. 2011a):

- (1) An efficient energy carrier with a highest energy density value per mass of 140 MJ/kg;
- (2) H₂ is an environmental benign fuel with a variety of applications, (i.e. environmental friendly vehicles, domestic heating, and stationary power generation), and
- (3) H₂ can be generated on site, therefore any system that requires an energy carrier can utilize H₂.

The photocatalytic H₂ generation from water is considered to be one of the most promising ways to generate H₂, owing to these features:

- A clean and perpetual resource of solar energy,
- It is an environmental safe technology without generation of undesirable by-products and pollutants, and
- H₂ energy is a storable form of solar energy which can be used to overcome the intermittent characteristics and seasonal variation of solar influx.

The activity of the catalysts plays an important role in the photocatalytic H₂ generation process (Centi and Perathoner 2009). To a certain extent these catalysts will dictate the application of photocatalytic H₂ energy (Kudo 2006, Hernández-Alonso et al. 2009).

TiO₂ is the most widely studied photocatalyst for water purification and clean energy generation, the potential of TiO₂ has attracted significant attention since it was first reported by Fujishima and Honda (1972). Recently, studied works have been focusing on using innovative technology and synthesis methods to improve the photocatalytic activities of TiO₂ (Kudo and Miseki 2009, Chen and Mao 2007, Chen et al. 2010a). Using the principles of natural photosynthesis process, it is possible to fabricate hierarchical structured TiO₂ catalyst with improved photocatalytic activity. Furthermore, porous microstructure with nano-scale building blocks has showed its capability to improve the photocatalytic activity of TiO₂. Hierarchical structured TiO₂ possesses the merits in improving the photocatalytic activity via favoring the light absorption capability, enlarging the specific surface areas and promoting mass transfer, and retarding the recombination of photogenerated electrons and holes.

Hence, this study focuses on the development of hierarchical TiO₂ nanorod spheres and its application in clean water and energy production. Starting from a commonly used hydrothermal method, a novel recipe was firstly prepared to synthesize

hierarchical TiO₂ nanorod spheres. The synthesized TiO₂ nanorod spheres were uniquely applied in a concurrent photocatalysis and membrane filtration system for water purification. However, using this hydrothermal method to synthesize TiO₂ nanorod spheres at large scale is a challenge due to its poor production rate and repeatability. Hence, a novel high temperature calcination method was developed to fabricate hierarchical TiO₂ nanorod spheres on large scale. In comparison to hydrothermal method, the high temperature calcination process was able to produce TiO₂ nanorod spheres on large scale and simultaneously to promote the crystallization of TiO₂ which improves its photocatalytic activity. Furthermore, hierarchical TiO₂ nanorod spheres synthesized by high temperature calcination are exposed with a large percentage of highly reactive facets. With these remarkably improvements to the photocatalytic activity of TiO₂, this demonstrates the efficiency of these TiO₂ nanorod spheres in clean water and energy generation.

1.2. Scope and Objective

For this study, TiO₂ nanorod spheres for simultaneous clean water production and energy generation will be synthesized through a low temperature hydrothermal method and a novel facile high temperature calcination method.

The objectives of the study are as follows:

- To synthesize TiO₂ nanorod spheres with excellent photocatalytic activity for simultaneous water purification and energy generation.

- To examine water purification efficiency of the synthesized TiO₂ nanorod spheres in an integrated membrane filtration set up
- To evaluate the structural consistency of the TiO₂ nanorod spheres on large scale by using the novel high temperature calcinations method
- To reveal the formation mechanism and to further evaluate the effect of calcination temperature and atmosphere on hierarchical TiO₂ nanorod spheres by using a variety of versatile analysis techniques;
- To compare the TiO₂ nanorod spheres from the two different methods (low temperature hydrothermal method and novel calcination method) and assess its potential applications in photocatalytic H₂ generation.

1.3. Organization of Study

This thesis comprises of eight chapters.

Chapter One provides an introduction to the study and general information of use of nanotechnology for water purification and energy generation. The objectives, scope and organization of the thesis are also included in this chapter.

Chapter Two presents the literature reviews on the development of TiO₂ photocatalysis for water purification and clean energy generation. The highlights of recent advances in synthesis of hierarchical TiO₂ photocatalysts and its limitations and application in clean water and energy generation will also be covered.

Chapter Three presents the methods used in the experimentation process and the materials.

Chapter Four to Seven focuses on the results and discussion of this study. Chapter Four will study in details the characteristics, formation mechanism and the multifunctional applications in water purification of the hierarchical TiO₂ nanorod spheres synthesized from low temperature hydrothermal method.

Chapter Five will subsequently analyze and discuss the experimental results obtained from hierarchical TiO₂ nanorod spheres synthesized through novel high temperature calcination method.

Chapter Six will systematically investigate the properties of hierarchical TiO₂ nanorod spheres and the effect of calcination temperature and atmosphere on its formation.

Chapter Seven presents the photocatalytic performances of hierarchical TiO₂ nanorod spheres for water purification and clean energy generation under the irradiation of UV light as well as a detailed comparison between the TiO₂ nanorod spheres synthesized from the two different methods

Finally, Chapter Eight comprises the conclusions of this study and recommendations for future research.

CHAPTER 2 LITERATURE REVIEW

2.1. Global Challenges from Water and Energy

Fresh and clean water are necessities to ensure survivability of human life and a nation's sustainable development. The availability of this valuable resource has been threatened due to the increase in global population, living standards and rapid industrialization and urbanization. This water crisis has affected different countries and districts throughout the world. As reported by the Organization of Economic Co-operation and Development (OECD) and United Nations (UN), approximately 0.35 million people in 25 different countries, particularly in the Middle East and Africa, are currently suffering from water shortage. Both the OECD and UN foresee that this number will grow to 3.9 billion from 52 countries by 2050.(Aldhous 2003b). Evidently, from the Environmental Sustainability Index (ESI) and Environmental Performance Index (EPI), the presence of safe and clean water resources is an important indicator used to assess a country's ability for sustainable development of her society and economy.

Besides, the need for safe and clean water resources, energy is also an important resource for sustainable development in today's society and economy. Every aspect of our economic, social and physical welfare depends on the sufficient and uninterrupted supply of energy. The European "World Energy Technology and Climate Policy Outlook (WETCPO)" had predicted that the global energy demand would increase at an average rate of 1.8 % per annum (Commission 2003). This

increase in demand is currently met by the reserves of fossil fuels, however the burning of fossil fuels and its associated products generates greenhouse gases and other pollutants which cause the global climate change (Davis et al. 2010). Despite these environmental implications, these non-renewable fossil fuels have been exploited severely and would be depleted in the next century. The depletion of fossil fuels has led to the surge in the price of global oil, thus this has led to the need to seek out alternative and clean energy.

For this reason, energy security and alternative clean energy exploitation issues have both become global topics of common concerns. In order to tackle the challenge of energy crisis, governments have begun to promote and encourage a new clean energy economy via prioritizing clean energy innovation and development (PEW 2010). Recently, various kinds of alternative clean energy have been developed with the purpose of discovering an ideal alternative energy source of fossil fuels (Turner 1999, 2004).

It is important to note that having a clean, safe, reliable and secure energy supply is the basic requirement for a competitive economic environment and sustainable high standard of living. According to the European Commission report, an ideal energy system must meet these lowering societal needs at an affordable price (Commission 2003):

- Mitigate the effects of climate change;
- Reduce toxic pollutants; and

- Plan for diminishing reserves of oil

However failure to meet these requirements will have negative impacts on the economy, environment and public health. In order to meet this stringent criterion, the energy supplied should be efficiently utilized and carbon-free energy sources should be used to meet this increase demand.

For this study, H₂ energy is considered as a potential energy carrier due to its high energy density value (140 MJ/kg) and its environmental benefits. H₂ can be produced by several techniques from a variety of hydrogen containing compounds such as fossil fuels, biomass, or even water (Chen et al. 2010a). From an environmental perspective, greenhouse gases emission can be achieved by capturing and sequencing CO₂ when deriving H₂ from hydrocarbons such as fossil fuels or biomass. Additionally, H₂ can also be derived from water thus reducing the challenges. Furthermore, with the use of solar energy, H₂ can be produced from water and thus making it an ideal candidate as a potential substitute for fossil fuels to produce clean alternative energy to address the global energy crisis.

2.2. Water Purification Technologies

The second industrial revolution greatly promotes the development of society and stimulates fast innovations of new technologies. The soaring growth of world population and the fast industrialization process without predictable planning and managing in a scientific and sustainable manner resulted in the present severe water

deterioration situation. At the moment, human beings have been realizing the seriousness of water deterioration and the importance to address these severe issues to leave a green and beautiful world to our generations, scientists and engineers have been devoting unremitting efforts to searching new technologies to purify wastewaters. Staring from the activated sludge process in the early stage of the 19th century, to the promising membrane technology developed in the middle of 20th century, till now the advanced oxidation processes and so on, human beings never lack of new technologies for water purification. But to date we are still trying to look for ideal technologies to purify wastewaters in a high efficient, environmental-friendly and energy conservative manner.

2.2.1. Conventional Technologies for Water Purification

Depending on the origin and occurrence of wastewater, different technologies have been developed to purify wastewaters containing different pollutants. In general, the conventional water treatment technologies include physical, chemical and biological methods.

Table 2.1 Types of Treatment Methods

TREATMENT METHODS	TECHNIQUES
Physical	<ul style="list-style-type: none">• Sand Filtration• Adsorption
Chemical	<ul style="list-style-type: none">➤ Coagulation/flocculation➤ Co-precipitation➤ Ion Exchange
Biological	<ul style="list-style-type: none">• Activated Sludge

The type of technologies used for removing pollutants in wastewater depends on the wastewater's composition. Particularly, traditional activated sludge process is commonly used for the removal of organics in wastewater with use of micro-organism. This process is still widely used in many countries for the treatment of municipal wastewater, which is rich in organic pollutants. However, these conventional technologies have disadvantages such as, narrowed suitability for various wastewaters, relatively low water treatment capability, low water quality thus making it hard to meet the stringent requirements of drinking water standard. Furthermore, these processes have been associated with secondary pollution issues, large footprint and high operational cost, which limit their applications. Therefore, the conflicts between severe water deterioration issues and high water quality demand resulting from modernization and urbanization have become harder and harder to reconcile.

2.2.2. Membrane Technology for Water Purification

Since its development in 1960's, membrane filtration technology have been greatly developed and broadly applied in various fields such as pharmacy and water purification (Giacomini et al. 2010). Due to the increase in water quality regulations and the decrease in availability of fresh water supplies globally, membrane technologies have played a crucial role in water treatment (Jacangelo et al. 1997). Significantly different from conventional water treatment technologies, membrane technology possesses several advantages including: (1) minimization of chemical used during purification, (2) wide suitability to wastewaters containing different kinds of pollutants, (3) high water quality due to its high rejection rate, (4) low

operational and maintenance costs, (5) easy and reliable performance system, (6) compact system reducing the footprint of water treatment plant, (7) one-step reduction or elimination of most contaminants in an efficient manner.

Therefore, membrane technologies have been employed to remove a wide range of contaminants in various wastewaters, such as seawater desalination process (Service 2006), disinfection of surface waters (natural and synthetic) (Elimelech and Phillip 2011, Di Zio et al. 2005, Greenlee et al. 2009), disinfection by-products (DBPs) control (Konieczny 1998) and clarification and removal of synthetic and inorganic chemicals (Jacangelo et al. 1997). Traditional low pressure-driven membrane such as microfiltration and ultrafiltration (MF/UF), and high pressure-driven membrane, nanofiltration (NF) and reverse osmosis (RO) have exhibited their promising futures in the fields of water treatment and seawater desalination (Shannon et al. 2008). However, these membranes processes are driven by hydraulic pressures, which are “energy intensive”. Moreover, membrane fouling due to accumulation of organic and inorganic pollutants in the pores or on the surface of membrane is also an issue that prohibits the breakthrough of membrane technology in various applications (Bai et al. 2010). Membrane fouling often results in increase of operational and maintenance costs as well as decrease of water quality and lifespan of the membrane (Semiat 2008, Hightower and Pierce 2008, Subramani et al. 2011).

Recently, a novel forward osmosis (FO) membrane has been developed for wastewater purification and seawater desalination (Bai et al. 2011a, Chung et al. 2012,

Liu et al. 2011b). The basic mechanism of FO membrane is to utilize the salt concentration differences across the membrane to carry out the separation process. Driven by the osmotic pressure difference across semi-permeable membrane, water passes through semi-permeable membrane without use of external energy (Cath et al. 2006). Therefore, by minimizing or removing the use of energy in membrane process, makes FO membrane a promising technology in water reclamation (Liu et al. 2011b).

However, the use of FO membrane is limited by: (1) fabrication of an ideal FO membrane which is extra-thin, highly porous, and hydrophilic to reduce membrane resistance to increase permeate flux, and (2) choice of an ideal draw solute with high osmotic pressure and easy separation (Bai et al. 2011a). Thus it has resulted in a rigorous debate over the merits of the “energy efficiency” of FO membrane and its shortcoming due to its limited water production capability (Elimelech and Phillip 2011, Chung et al. 2012).

2.2.3. Photocatalytic Degradation for Water Purification

Natural organic matters (NOMs) are ubiquitous in surface and ground water sources like rivers, reservoirs, and so forth drinking water sources. Due to its complex composition and wide molecular weight distributions, treatment of NOMs is challengeable by using conventional water treatment methods. Moreover, if membrane filtration is employed for NOMs removal, operational problems such as severe membrane fouling would arise.

However, membrane technologies only provide a temporary solution to pollutant control as it only transfers these pollutants into a concentrated form such as waste sludge which requires further treatment and disposal. In addition, pressure-driven membrane filtration requires large amount of energy. Hence, there is an urgent need to search for alternative novel cost-effective technologies to not only remove NOMs but also generate clean energy from water. The waste sludge from these membrane processes has also been associated with secondary pollution. Ideally, NOMs and other organic pollutants in wastewaters should be completely degraded into CO_2 and H_2O in order to eliminate secondary pollution as well (Mills et al. 1993, Hoffmann et al. 1995).

One such approach is the use of UV illumination to excite electrons and holes from the surface of solid semiconductors. These excited electrons and holes would oxidize organic pollutants or water (H_2O) thus forming reactive oxidation species (ROS) such as $\text{OH}\cdot$ and $\text{O}_2\cdot$, which have the potential to further degrade organic pollutants. This degradation mechanism, known as photocatalysis would be explained in details in the later section of the thesis.

This approach of photocatalytic water purification using semiconductor have attracted a great deal of interests from both academic research and practical engineering. The significant interest in photocatalytic water purification can be

attributed to: (1) clarified effluent is harmless to environment, (2) the photodegradation process can be easily controlled by turning on/off the illumination source, and (3) the photocatalysis has the potential to be incorporated into existing UV water purification process to improve the water quality by disinfection of bacteria and mineralization of the refractory trace organics (Mills et al. 1993, Hoffmann et al. 1995).

The future of water purification using semiconductor based photocatalysis is dependent on the activity of photocatalyst. In the past decades, huge amount of research is focused on synthesis and development of novel and high efficient photocatalyst. The advances of nanotechnology and nanomaterials have driven the development of photocatalysis. Several semiconductor based photocatalysts have been developed for water purification in recent years (Chen and Mao 2007, Pan et al. 2010, Pan et al. 2008). However, studies are still necessary before semiconductor based photocatalysis can showcase its potential for water purification in an industrial and practical scale.

2.2.4. Development of Membrane-Based Water Purification Technologies

A model membrane process should have several unique features such as, high selectivity (good permeate quality), high permeate flux (high water production capability) and no or low membrane fouling potential (energy conservative). These aims can be achieved either through technology innovation or synthesis of innovative membranes.

Recent studies from Pendegast and Hoek (2011), have shown that water treatment ability of conventional ceramic and polymer membrane can be enhanced with the use of nanotechnology. Many novel membranes with excellent performances have been developed. For example, a filtration membrane made of cross-linked proteins which are mechanically robust and contain channels with diameters of less than 2.2 nm were reported to exhibit ultrafast permeation of water (Peng et al. 2009). Compared to traditional polymer membrane, vertically aligned carbon nanotube based membrane holds the great possibility for gas separation with high flux (Sholl and Johnson 2006, Hinds et al. 2003). The filtration performance of membrane can be further enhanced using an ultrathin porous silicon membrane (Striemer et al. 2007) or by immobilizing carbon nanotubes in silicon nitride (Hinds et al. 2003, Holt et al. 2004) or polymer films (Holt et al. 2006).

In addition, several other novel studies have shown the significant development of membrane based water purification technology. In order to prevent the decline of permeate flux, Zhang et al. (2008a) developed a novel TiO₂ nanowire membrane for concurrent water purification and photodegradation of organic fouling. Also, a study by Ke et al. (2007), showed that a high performance ceramic membrane with high flux can be fabricated through a novel concept of building up a selective layer of randomly orientated TiO₂ nanofibers.

A self-organized, dense and free standing membrane consisting of vertically oriented, both-side-open TiO₂ nanotubes, was reported to allow direct, size-selective, flow-through photocatalytic reactions with very high efficiency (Albu et al. 2007, Albu et al. 2008). However, this TiO₂ nanotubes membrane is too small and fragile to be applied for practical applications.

A new type of membrane with an asymmetric film geometry consisting of a thin nanoporous layer and a supporting membrane was developed for the removal of viruses at a high flux and ultra-high selectivity (Yang et al. 2006).

Inspired by natural phospholipid membrane in human tissue organization, a phospholipid nonwoven membrane was fabricated by versatile electrospinning method. This membrane exhibited high permeate flux and good selectivity (Mckee et al. 2006).

The technology innovation is achieved through incorporating membrane with other technologies such as photocatalysis, or conventional water treatment processes to reduce the fouling formation potential. The hybrid membrane and photocatalysis system is a “*win-win*” strategy to maximize these advantages of photocatalysis and membrane filtration and to minimize their disadvantages (Bai et al. 2009, Bai and Sun 2011). In the concurrent photocatalysis and membrane filtration system, a multifunctional layer is newly created on the surface of membrane with the assembly

of hierarchical TiO₂ nanorod spheres. On the one hand, the functional layer is able to degrade the organic pollutants in wastewater so as to avoid the formation of membrane fouling, on the other hand the porous functional layer is easy for water passing through so as to maintain membrane filtration at a constant high flux state (Bai et al. 2010, Huang et al. 2008). Another hierarchically structured and multifunctional membrane was fabricated via integrating the advantages of conventional polymer membrane as supporting layer and “forest” like hierarchically structured TiO₂/ZnO nanomaterials as functional layer. This membrane showed multifunctional properties for water purification, such as high photodegradation ability, high flux and high antibacterial capacity, which makes it as a good candidate to tackle the challenge of producing clean water at a constant high flux with no membrane fouling and energy saving manner. The outstanding performance of this novel membrane would bring enough benefits to membrane filtration industry for clean water production and environmental protection (Bai et al. 2012a).

2.3. Clean Hydrogen Energy Generation

2.3.1. Traditional Clean Energy

Facing the challenges of global energy crisis, efforts have been undertaken to search for new and renewable energy (Turner 1999, Pegels 2010, Verbruggen et al. 2010). Table 2.2 summarizes, the potential and status of some of typical renewable energy (Grossmann et al. 2010).

Table 2.2 Potential and status of renewable energy technologies (Kreith and Goswami 2007)

Technology	Annual Potential	Operating Capacity 2005 ^{a,b}	Investment Costs U.S.\$ per kW ^b	Current Energy Cost	Potential Future Energy Cost
Biomass Energy	276-446 EJ total or 8-13 TW MSW~6 EJ				
Electricity		~44 GW	500-6000/kW _e	3-12c/kWh	3-10c/kWh
Heat		~225 GW _{th}	170-1000/kW _{th}	1-6c/kWh	1-3c/kWh
Ethanol		~36 bln L	170-350/kW _{th}	25-75c/L(ge) ^c	6-10\$/GJ
Biodiesel		~3.5 bln L	500-1000/kW _{th}	25-85c/L(de) ^d	10-15 \$/GJ
Wind Power	55 TW theoretical 2 TW practical	59 GW	850-1700	4-8 c/kWh	3-8 c/kWh
Solar Energy		>100 TW			
Photovoltaics		5.6 GW	5000-10,000	25-160 c/kWh	5-25 c/kWh
Thermal power		0.4 GW	2500-6000	12-34 c/kWh	4-20 c/kWh
Heat			300-1700	2-25 c/kWh	2-10 c/kWh
Geothermal	600,000 EJ useful resource base 5000 EJ economical in 40-50 years		300-1700	2-25 c/kWh	2-10 c/kWh
Electricity		9 GW	800-3000	2-10 c/kWh	1-8 c/kWh
Heat		11 GW _{th}	200-2000	0.5-5 c/kWh	0.5-5 c/kWh
OCEAN ENERGY					
Tidal	2.5 TW	0.3 GW	1700-2500	8-15 c/kWh	8-15 c/kWh
Wave	2.0 TW		2000-5000	10-30 c/kWh	5-10 c/kWh
OTEC	228 TW		8000-20,000	15-40 c/kWh	7-20 c/kWh
Hydroelectric	1.63 TW theoretical				

Large	0.92 TW econ.	690 GW	1000-3500	2-10 c/kWh	2-10 c/kWh
Small		25 GW	700-8000	2-12 c/kWh	2-10 c/kWh

Note: ^a GWe, gigawatt electrical power.

^b GWth, gigawatt thermal power.

^c ge, gasoline equivalent liter.

^d de, diesel equivalent liter.

2.3.2. Photocatalytic H₂ Generation

Photocatalysis is expected to make a great contribution to both environmental purification (emission degradation and water purification) and renewable energy generation. H₂ energy is widely considered to be the future clean energy carrier in many applications, such as environmentally-friendly vehicles, domestic heating, and stationary power generation. Photocatalytic H₂ generation from water is one of the most promising ways to realize a H₂ economy for three reasons: (1) this technology is based on photon (or solar) energy, which is a clean, perpetual source of energy, and many water, which is a renewable resource; (2) it is an environmentally safe technology without undesirable by-products and pollutants; and (3) the photochemical conversion of solar energy into a storable form of energy, i.e. H₂, allows one to deal with the intermittent character and seasonal variation of solar influx (Zhu and Zach 2009).

2.4. TiO₂ Based Photocatalysis

2.4.1. Introduction of TiO₂ Based Photocatalysis

Since the first discovery by Fujishima and Honda in 1972 reporting the successful water splitting via a UV light illuminated solid TiO₂ (Fujishima and Honda 1972), enormous efforts have been devoted to the research of TiO₂. Owing to its unique

properties such as physicochemical stability in solution, high photocatalytic activity for degradation of pollutants and organic matters under the irradiation of UV light, TiO₂ has become one of the most widely studied semiconductor materials.

In the past decades, an increasing number of publications regarding TiO₂ has been emerging at an unprecedented rate in a variety of applications such as catalysis (Pan et al. 2010), optical storage and transfer, sensor design (Li et al. 2008), pigment production (Mills et al. 2010), corrosion protection, optical coating, ceramic manufacturing (Ke et al. 2007), electric device design (Krishnamoorthy et al. 2011), water purification (Bai et al. 2010), self-cleaning coatings (Nakajima et al. 2000) and hydrophobic/hydrophilic surface (Feng and Jiang 2006, Feng et al. 2005) as a result of its electronic, magnetic, optical, chemical and mechanical properties (Hoffmann et al. 1995).

2.4.1.1. Basics of Photocatalysis

Since the development of TiO₂, researchers have tried to explain the basic mechanism of photocatalysis. As explained by Hoffman in 1995 (Hoffmann et al. 1995), the mechanism is elaborated in Figure 2.1.

Figure 2.1 Primary steps photoelectrochemical mechanism. (1) formation of charge carriers by a photon; (2) charge carrier recombination to liberate heat; (3) initiation of an oxidative pathway by a valence-band hole; (4) initiation of a reductive pathway by a conduction-band electron; (5) further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products; (6) trapping of a conduction-band electron in a dangling surficial bond to yield Ti(III); (7) trapping of a valence-band hole at a surficial titanol group. (Hoffmann et al. 1995)

The electron-hole pair is generated on the surface of TiO_2 after it is excited by UV light, while the formation of ROS is the key for final mineralization of organic pollutants into CO_2 and so on. As photocatalytic reaction always occurs in the presence of air or oxygen acting as the primary electron acceptor, and consequently the hydrogen peroxide would form on the surface. Hydroxyl radicals are formed on the surface of TiO_2 by the reaction of $h\nu_{\text{VB}}^+$, with adsorbed H_2O , hydroxide, or surface titanol groups ($>\text{TiOH}$) as shown in Figure 2.2.

Figure 2.2 Secondary reaction with ROS in photoelectronchemical mechanism. (Hoffmann et al. 1995)

The lifespan (or the separation time of photogenerated electrons and holes) is of significant importance to determine photocatalytic activity, because the photogenerated electron-hole pair needs sufficient time to migrate to and finally mineralize the adsorbed pollutants on the surface of catalysts. However, the fast recombination of electrons and holes before mineralizing pollutants in a very short time will deactivate the catalysts (Linsebigler et al. 1995a). Upon excitation, the fate of separated electron and hole can follow several pathways, which is summarized in Figure 2.3 (Linsebigler et al. 1995a).

Figure 2.3 Schematic photo-excitation in a semiconductor solid followed by de-excitation events. (Linsebigler et al. 1995a)

The photogenerated electron is transferred from the surface of catalyst to the adsorbed organic /or inorganic species /or to solvent. The electron transfer process is more efficient if the species are pre-adsorbed on the surface of catalyst. While the catalyst can donate electrons from its surface to reduce an electron acceptor (usually oxygen in an aerated solution) (Pathway C); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (Pathway D). The probability and rate of the charge transfer processes for electrons and holes edges depends on the respective positions of band edges for the conduction bands (CB), valence bands (VB) and the redox potential levels of the adsorbed species. It is the recombination of electrons and holes that is in competition with charge transfer to adsorbed species. Recombination of the separated electrons and holes can occur in the vacancy of catalyst (Pathway B) or on the surface (Pathway A) resulting in the release of heat. The place of back-donation after charge transfer from adsorbed species to catalyst surface can occur but is not illustrated in Figure 2.3.

2.4.1.2. Basic Mechanism of Photocatalytic H₂ Generation

Figure 2.4 TiO₂ based photocatalytic water splitting H₂ generation with the presence of methanol using as the sacrificial reagent. (Linsebigler et al. 1995a)

Using the basics of photocatalysis, the mechanism of TiO₂ photocatalytic water splitting H₂ generation with the presence of methanol as sacrificial reagent is proposed in Figure 2.4. When the energy of incident light is larger than the bandgap, electrons and holes are generated in the CB and VB of catalysts, respectively. The photogenerated electrons and holes cause reduction and oxidation (redox) reaction similarly to electrolysis. Water molecules are reduced by electrons to form H₂ and are oxidized by holes to form O₂ in water splitting process. The produced H₂ and O₂ has a great potential to reversibly react into H₂O, therefore in order to improve the photocatalytic H₂ generation activity with the use of a sacrificial reagent such as methanol. These reagents are used to scavenge the holes to prevent the reversible reaction from H₂ to H₂O. The end product from the scavenging of holes is the mineralization of methanol into CO₂ and H₂O (Kudo and Miseki 2009).

Furthermore, it is of great significance to choose suitable photocatalyst for water splitting H_2 generation by theoretically evaluating the bandgap and levels of the CB and VB. The bottom level of CB has to be more negative than the redox potential of H^+/H_2 (0 V vs. NHE). On the contrary, the top level of VB has to be more positive than the redox potential of O_2/H_2O (1.23 V). In view of this, the theoretical minimum bandgap for water splitting is therefore 1.23 eV which corresponds to light of about 1100 nm (Kudo and Miseki 2009, Gratzel 2001).

2.4.2. Improvement of the TiO_2 Photocatalytic Activity

As an alternative and green technology, TiO_2 photocatalytic reaction has demonstrated its potential to be a promising technology for emerging environmental purification and energy generation. However, the broad application of TiO_2 photocatalysis is greatly limited by its relatively low photocatalytic activity. Hence, significant research efforts were devoted to improving the photocatalytic activity of TiO_2 . To achieve this aim, four major strategies can be summarized.

First, the effective surface area has to be maximized (Fonzo et al. 2009), underlying the philosophy of '*the importance of nothing and the unimportance of periodicity*' in catalytic nano-architectures, where '*nothing*' is the porosity at the nanoscale (Rolison 2003). Second is the shifting of the absorption limit of material in the visible range, with the aim to maximize the light absorption efficiency due to the large bandgap of TiO_2 . Third is to effectively suppress the recombination of electrons and holes (Liu

et al. 2007a). As photocatalytic activity is dominated by the lifespan of electrons and holes generated after the photocatalyst is excited by light irradiation, hence effective suppression of the recombination would increase the performance of photocatalyst. The fourth strategy is to synthesize single crystal TiO_2 with large percentage exposed highly active facet (Yang et al. 2008).

2.4.2.1. Large Specific Surface Area

Photocatalytic reactions in heterogeneous system occur at close proximity to the light illuminated surface of solid photocatalyst. However, recent studies have shown that photocatalytic reaction can also occur at distances remote (tens of micrometers) from the illuminated surface through the diffusion of reactive species in air or solution phase or on the surface (Fujishima et al. 2007, Fujishima et al. 2000). Nevertheless, photocatalytic reaction can still be said to be a surface-dominated reaction, the efficiency of which is greatly dependent on the surface area of photocatalyst (Fujishima et al. 2008). By increasing the surface area of photocatalyst, it will provide more reaction sites which promote mass transfer thus improving the photocatalytic activity.

Materials properties largely depend on the presence of accessible pores and pore size. Particularly in heterogeneous photocatalysis system, a direct correlation is observed between the photocatalytic performance and the microstructure of photocatalyst (Pan et al. 2010). Porous structured catalysts with large specific surface area have a positive effect on the improvement of photocatalytic activity, which is ascribed to two advantages: (1) large specific surface area would provide more reaction sites and

promote mass transfer between solid and liquid phase in the heterogeneous photocatalytic reaction system, and (2) porous structure is beneficial for the enlargement of specific surface area and providing more accessible pores for reactants. Therefore, the search for new catalysts with an appropriate crystal structure and large specific surface area has been intensively pursued (Pan et al. 2010). Pore sizes are classified according to the IUPAC as micropores, mesopores and macropores. Microporous materials contain pores which are predominately below 2 nm whilst mesoporous materials contain pores with diameters between 2 nm and 50 nm, whereas macroporous materials have pores with diameters larger than 50 nm (Rolison 2003). For pores exceeding several hundreds of nanometers, materials are most often classified as nonporous (Zhai et al. 2011). Generally, the wide application of porous photocatalysts in water purification and clean energy generation mainly lies in three aspects: (1) high density of active centers for surface-dominated photocatalytic reactions (Fujishima et al. 2008), (2) enhanced light harvesting capability via allowing more light reflection and multiple scattering in the pores (Bai et al. 2010), and (3) recovery and possible reuse after each cycle of photocatalytic process.

2.4.2.2. Enhanced Light Absorption Capability

Figure 2.5 Solar spectrum at sea level with the sun at zenith (Linsebigler et al. 1995a)

The effectiveness of light-driven photocatalytic process to obtain clean energy and perform water decontamination is dictated to certain extent by the photocatalyst's capability of absorbing light (Chen et al. 2011a). However, the large bandgap of TiO_2 (3.2 eV for anatase, 3.0 eV for rutile) greatly restricts its ability to generate electron-hole pair for photocatalysis under UV illumination. The solar spectrum in Figure 2.5 (Linsebigler et al. 1995a) shows that UV light only accounts about 4 % of the overall solar intensity. Therefore, the enhancement of light absorption capability can be achieved via several routes as reported below.

Hierarchical structure. The high photosynthetic efficiency of natural forest via efficiently utilizing solar light inspires the novel research of hierarchical structured TiO_2 nanomaterials (Fonzo et al. 2009, Zhou et al. 2010). Novel hierarchical structured TiO_2 nanomaterials with multi-scaled organizations hold the potential to

permit better light reflection and absorption inside interiors so as to enhance the light absorption capacity thus improving the photocatalytic activity (Bai et al. 2010, Pan et al. 2008).

Well crystallized TiO₂. There is a direct correlation between the light reflection index and the crystallization of TiO₂ (Hamadanian et al. 2010). Well crystallized TiO₂ has a higher potential in its light absorption capability. In comparison to amorphous TiO₂, TiO₂ crystal including anatase, rutile and brookite displays higher light absorption capacity, which is beneficial for the high photocatalytic activity.

Elemental doping. TiO₂ doped with transition metals or inorganic elements (such as C, S, N, B, and F) were reported to be able to enhance the light absorption capability for high photocatalytic activity (Asahi et al. 2001, Pan et al. 2011, Shao et al. 2008, Sun et al. 2008, Xu et al. 2010a, Yu et al. 2005). The doped inorganic element would act as electron donor or acceptor in the forbidden band of TiO₂, thus inducing absorption in the visible region (Xu et al. 2010b). It has been reported that light absorption enhancement of TiO₂ have been achieved through successfully doping of N into the substitutional sites of TiO₂. This narrows the bandgap of TiO₂ so as to improve the photocatalytic activity (Asahi et al. 2001).

2.4.2.3. Anti-recombination of Photogenerated Electrons and Holes

Metal Doped TiO₂

Fujishima and Honda reported that a noble metal doped TiO_2 (Pt/TiO_2) greatly enhanced the reactivity for photoconversion of H_2O into H_2 and O_2 (Fujishima and Honda 1972). After excitation the generated electrons migrate to noble metal to suppress its recombination with holes, thus enhancing its photocatalytic activity. Additionally, as a result of its own catalytic property the doped metal also modifies the photocatalytic properties of TiO_2 by changing the distribution of electrons. When the two species come in contact, the Fermi levels of metal and TiO_2 would cause electrons to flow to TiO_2 from metal. The decrease in electron density within the TiO_2 leads to an increase of the hydroxyl group acidity, which in turn affects the photocatalytic activity occurring on the surface of TiO_2 (Linsebigler et al. 1995a).

TiO_2 Coupled with Other Semiconductors with Different Bandgaps

The coupling of TiO_2 with another semiconductor provides an attractive way to increase the photocatalytic activity of TiO_2 by increasing the separation time of electrons and holes (Bai et al. 2012a). The mechanism of the separation of electrons and holes lies in the different bandgaps between TiO_2 and the coupled semiconductor. When a semiconductor (e.g. ZnO , SnO_2) with a higher CB is coupled with TiO_2 , the electrons generated after excitation on the semiconductor would transfer to TiO_2 to enrich the electron density on TiO_2 . While the holes generated on TiO_2 will transfer to the coupled semiconductor. The manner, in which the electrons and holes are effectively separated, causes the increase in the photocatalytic activity of the coupled system than TiO_2 alone (Bai et al. 2012a, Cao et al. 2000).

Furthermore, when TiO_2 is coupled with a semiconductor (e.g. CdS , $E_g \sim 2.5 \text{ eV}$) with a narrower bandgap and a higher CB than TiO_2 , an illumination source with a smaller energy is able to directly excite the coupled semiconductor to generate electrons, with the holes remaining in the VB of coupled semiconductor (Girginer et al. 2009, Lee et al. 2009, Tada et al. 2006, Zhu et al. 2009, Yu et al. 2003). These electrons then migrate to TiO_2 to increase the charge separation thus improving the photocatalytic activity of TiO_2 . Such a semiconductor coupled TiO_2 system not only improves the separation of electrons and holes, but also holds great potential to utilize illumination sources in the visible range for photocatalysis.

Non Metal Doping on TiO_2

Non metal elements such as C, N (Aman et al. 2010, Liu et al. 2009), F and S doped on TiO_2 not only act as the electron acceptor or donor in the forbidden band of TiO_2 , it also induces absorption in the visible region and possesses a certain potential to serve as surface trap state for the photogenerated electrons or holes. Therefore, the inorganic element doped TiO_2 is of great importance for suppressing the recombination of electrons and holes to favor high photocatalytic activity (Yu et al. 2005, Xu et al. 2010b, Xiang et al. 2011) .

Hierarchical Structured TiO_2

Besides the above-mentioned techniques, hierarchical structure also adds another merit for TiO_2 to suppress the recombination of electrons and holes via efficiently promoting electrons transfer. Structured TiO_2 nanomaterials with multi-scaled

organizations promote mass transfer and simultaneously enhance electron transfers, resulting in the recombination of electrons and holes (Bai et al. 2010, Fonzo et al. 2009, Zhou et al. 2010).

2.4.2.4. Exposure of Highly Reactive Facet

TiO₂ exists in three crystal phases: rutile, anatase and brookite. The relationship between the size and the stability of various TiO₂ phases as reported in recent studies, states that TiO₂ in rutile phase is the most stable phase for particles above 35 nm in size. TiO₂ in anatase is the most stable phase for nanoparticles below 11 nm. Whereas, the brookite is the most stable phase for nanoparticles in the 11-35 nm range (Fujishima et al. 2008). Although different TiO₂ phases have different activity for photocatalytic reactions, majority of the practical works have been carried out with either rutile or anatase TiO₂ (Linsebigler et al. 1995a). The crystal structures of rutile and anatase TiO₂ can be described in terms of chains of TiO₆ octahedral as shown in Figure 2.6. The two crystal structures differ by the distortion of each octahedron and the assembly pattern of the octahedral chains. Each Ti⁴⁺ ion is surrounded by an octahedron of six O²⁻ ions. The octahedron in rutile is not regular, thus its slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. Furthermore, the Ti-Ti distances (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile) in anatase is greater than the Ti-O distances (1.934 and 1.980 Å in anatase vs 1.949 and 1.980 Å in rutile) in rutile phase. In the rutile structure each octahedron is in contact with 10 neighboring octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in the anatase structure, each octahedron is in contact with eight neighbor octahedrons (four

sharing an edge and four sharing a corner). These differences in lattice structure between the two phase of TiO_2 results in the difference in mass densities and electronic band structures (Linsebigler et al. 1995a).

Figure 2.6 Structure of rutile and anatase of TiO_2 . (Linsebigler et al. 1995b)

Rutile TiO_2 has three main crystal facets, the (110) and (100) facets which are quite low in energy and thus is considered to be important for practical applications. The (001) facet is thermally less stable, which is restructured above 475°C (Fujishima et al. 2008).

The surface stability and reactivity of a single crystal TiO_2 plays a dominant role in the efficiency of photocatalytic reaction occurring on the surface of solid catalysts (Fujishima et al. 2008). Under normal circumstances, most of the surfaces of TiO_2 are covered by thermodynamically stable facets. It is reported by Lazzeri et al. (2001) that the thermodynamically stable (110) facet accounts for more than 94 percent of

the total surface of anatase TiO_2 , which results in low photocatalytic activity because of its low reactive facets.

Yang et al. (2008) reported that the single crystal anatase TiO_2 cubic exposed with high percentage of reactive (001) facets exhibited high photocatalytic activity. However, other researchers also claimed that theoretically anatase (100) facets are more active and accordingly exhibit higher catalytic activity than (001) and (101) facets (Li and Xu 2010). Though it is still debatable which facet is the most active facet for anatase TiO_2 , researchers are beginning to develop a single crystal anatase TiO_2 with highly reactive facets to enhance the photocatalytic activity (Li and Xu 2010, Feng et al. 2011, Liu et al. 2010a, Liu et al. 2010b, Wang et al. 2011).

Similar to anatase TiO_2 , rutile TiO_2 also has three major facets ((110), (100) and (001)) which affects its performance in photocatalytic reaction (Diebold 2003), however lesser reports were found about the single crystal rutile TiO_2 with exposed high energy surface. Recently, single crystal (110) facet exposed rutile TiO_2 nanorods were prepared by reacting sodium titanate with hydrochloric acid and exhibited high photocatalytic activity (Ke et al. 2009). The single crystal rutile TiO_2 nanorods were synthesized to grow along the [001] direction, while the circumferential facets are (110) facet which is identified as the photoactive facets of rutile TiO_2 . The highly exposure of photoactive (110) facet would promote its photocatalytic performances. Well faceted rutile TiO_2 nanorods with regular geometric configuration were also hydrothermally prepared by chemical modification of TiCl_4 by ethylene glycol to

slow down the reactivity of precursor toward water (Xiong et al. 2010). Such method results in the single crystal rutile TiO_2 nanorods growing along [001] direction and with circumferential (110) reactive facets surrounded, to lead to the improvement of photocatalytic activity.

2.4.3. Hierarchical Structured TiO_2 Photocatalysts and its Significance

2.4.3.1. Definition of Hierarchical Structure

Inspiration

As a highly complex, multi-disciplinary and multifunctional system, nature is indeed a school for materials scientists to synthesize lots of novel materials applied in a variety of fields, because the sophistication, miniaturization and hierarchical organizations of nature are the inexhaustible source of inspiration for scientists (Sanchez et al. 2005).

The natural photosynthesis process in conversion photo energy to chemical energy provides an example to improve the photocatalytic activity with hierarchical structured catalysts. Typically featured with a hierarchical and self-organized superstructure starting from the single tree with trunks, branches and leaves, up to the entire forest assembly, the forest maximizes the gaseous exchange with atmosphere by maximizing leaf area, and optimizing leaf exposure to sunlight. From this point of view, the hierarchical structure with multi-scaled organizations providing large and accessible surface area would be desirable for the photocatalytic reactions (Fonzo et al. 2009).

Features of Hierarchical Structured Photocatalysts

- Multi-scaled organizations at different scales from nanometers to millimeters (Fonzo et al. 2009)
- Each construction at different scales allows the material to fit the physical or chemical demands occurring at these different levels (Vall é et al. 2006)

2.4.3.2. The Significance of Hierarchical Structure on the Improvement of Photocatalytic Activity

The hierarchical structure of photocatalyst plays a great significance in the improvement of photocatalytic activity. In the past decades, increasing number of publications have demonstrated the significance of hierarchical structured catalysts in the improvement of photocatalytic activity, which are summarized as follows (Rolison 2003, Sanchez et al. 2005, Soler-Illia et al. 2002):

- Hierarchical structure is able to maximize the specific surface area within small footprint;
- Hierarchical structure is favorable for enlarging the light absorption capability by permitting more light reflection and multiple scattering inside the interior;
- Hierarchical structure is able to retard the recombination of photogenerated electrons and holes via promoting the electrons transfer;

The above-mentioned advantages from hierarchical structure will benefit the improvement of photocatalytic activity of photocatalysts.

2.5. The Development of Hierarchical Structured TiO₂ Photocatalysts

Hierarchical structure comprises with multi-scaled organizations at different measurable scales. TiO₂ photocatalysts have been well studied, particularly on TiO₂ photocatalysts with different shapes such as nanoparticles (Teleki et al. 2010), nanospheres (Bai et al. 2010, Yang and Zeng 2004), nanorods (Bae et al. 2009, Cottam and Shaffer 2007, Liu et al. 2007b), nanowires (Yang et al. 2010), nanotubes (Albu et al. 2008, Grimes 2007), and nanofibers (Chungchote et al. 2009, Ostermann et al. 2006) etc. However, among these TiO₂ photocatalysts, only porous or hollow nanospheres possess the basic characteristics of hierarchical structure with multi-scaled organizations. The distance between different nanospheres is in the range of micrometer scale, while the porous dimension inside the spheres is in nanometer scale (Pan et al. 2010, Pan et al. 2008, Hu et al. 2011, Lou et al. 2008).

Hierarchical porous TiO₂ photocatalysts built up with well-defined building blocks at nano- and meso- scopes exhibited large specific surface area as a result of controllable morphology at various length scales (Pan et al. 2010, Liu et al. 2011c). Besides the large specific surface area, hierarchical porous TiO₂ photocatalysts also greatly promotes the rapid reactants transport through the porous structure, smaller pores provide sites for adsorption/desorption and allowing catalytic reactions to occur (Liu et al. 2011c). Meanwhile the microstructure with porous TiO₂ spheres would also permit more light absorption and multiple scattering inside its interior (Pan et al. 2008).

Comparing hierarchical TiO₂ nanorod to other porous TiO₂ photocatalysts, TiO₂ nanorods possess the regular building blocks (Bai et al. 2010). Furthermore, one-dimensional (1D) TiO₂ nanorods possess another benefit as it promotes the electron transfer due to its large aspect ratio (length: diameter). These advantageous properties contribute to the improvement of photocatalytic activity for water purification and clean energy generations.

2.6. Synthesis of Hierarchical TiO₂ Nanorod Spheres

2.6.1. Synthesis of Rutile TiO₂

TiO₂ with different crystal phase has different physicochemical properties such as refractive index, chemical reactivity and stability, and photochemical reactivity, (Tahir et al. 2006). Anatase TiO₂ is widely applied in a variety of fields such as photocatalysis, dye-sensitized solar cells (DSSC) due to its better electrochemical performance than rutile TiO₂. However, the rutile TiO₂ still has some advantages over anatase such as high optical stability, high chemical stability, high refractive index, excellent light scattering efficiency favorable for light harvesting, super photocatalytic properties, and cheaper production cost (Kim et al. 2002, Thiele and French 1998).

In view of TiO₂ fabrication, rutile TiO₂ is harder to be synthesized in a comparison to anatase TiO₂, which is easy to be produced at low temperature condition (Aruna et

al. 2000). In general, three synthetic routes have been developed for the synthesis of rutile TiO_2 . The first route is the use of a sol-gel method by hydrolyzing titanium alkoxides. Both titanium ethoxide (Slunecko et al. 1998) and titanium tetraisopropoxide (TTIP) (Terabe et al. 1994) have been reported to hydrolyze into rutile TiO_2 through well prepared sol-gel method. However, high temperature ($>500\text{ }^\circ\text{C}$), long-term aging at room temperature or exposure to high relative humidity are still necessary for the successful formation of rutile TiO_2 . Furthermore, the sol-gel method makes it hard to synthesize TiO_2 with well-tailored microstructure and may lead to the aggregation of TiO_2 which hinders the surface reactions (Hosono et al. 2004).

The second approach is the hydrolysis of inorganic salts such as TiCl_4 in an aqueous solution (Cheng et al. 1995, Kim and Sanders 1999). This reaction would take place both under hydrothermal or moderate conditions (Komarneni et al. 1999). The hydroxylation of TiCl_4 both can produce rutile and anatase TiO_2 depending on the synthetic conditions. For example, the acid-base conditions of the aqueous solution affects the crystal phase of final produced TiO_2 . Strong acidic aqueous solutions is in favor of the formation of rutile TiO_2 (Tahir et al. 2006) while a strong basic aqueous mixed solution with the presence of other components such as block copolymer or sulfate ions would result in anatase TiO_2 (Kim et al. 2002). Same as sol-gel method, the hydroxylation of TiCl_4 is available for the preparation of rutile TiO_2 fine powder, no report of TiO_2 with microstructure was found to date (Hosono et al. 2004).

The third approach was recently developed to synthesize rutile TiO_2 films by heterogeneous nucleation reactions occurring in NaCl supersaturated aqueous Ti(IV) solution. Different from the previous two approaches, this method allows the synthesis of hierarchical rutile TiO_2 in the form of nanorod or nanothorns (Liu and Aydil 2009). Using this method, it has been reported that the successful synthesis of TiO_2 nanorods, nanoneedles or nanopins grown on substrate films like borosilicate glass slides, silica wafers, polypropylene, polystyrene, poly(ethylene terephthalate) (Yamabi and Imai 2002), displays a super switchable hydrophobic ability (Feng et al. 2005, Hosono et al. 2004, Yamabi and Imai 2002, Hosono et al. 2005). Other researchers also showed that single crystalline rutile TiO_2 nanorods growing on Fluoride-doped Tin Oxide (FTO) substrates, exhibit comparable performance in DSSC (Liu and Aydil 2009). However to date few publications are found to have reported on the fabrication of hierarchical TiO_2 nanorods using this method.

2.6.2. Hydrothermal Methods for the Synthesis of TiO_2 Nanorod Spheres and its Limitation

TiO_2 nanorods are the basic building units for TiO_2 nanorod spheres, and hydrothermal method is a popular approach used for the synthesis of TiO_2 nanorods. Hosono et al, reported the formation of TiO_2 nanorod spheres growing on glass slides using a well-tuned hydrothermal method (Feng et al. 2005, Hosono et al. 2004, Hosono et al. 2005). In this synthetic route, the glass slide is an important substrate, as it is postulated that the nucleation of TiO_2 nanorods would initially occur on some spots of glass slide and subsequent crystal growth proceeded in the radial direction of bulk solution leading to the formation of TiO_2 nanorod on the surface of glass

slides. Besides the important function as substrate glass slide, the anion (Cl^-) plays a dominant role in determining the growth direction of TiO_2 nanorods, as Cl^- is reported to enable the growth of nanorods with an aspect ratio varying with the concentration of Cl^- (Filankembo et al. 2003). When the Cl^- is adsorbed on the (110) plane of rutile TiO_2 , the growth of TiO_2 can be suppressed and accelerated in the [110] and the [001] direction, respectively (Cheng et al. 1995). The reported TiO_2 nanorod spheres growing on the surface of glass slides showed superhydrophobic/hydrophilic properties (Feng et al. 2005, Wang et al. 1997). However, when the TiO_2 nanorod spheres were used as photocatalysts, its merits were lowered greatly as the hierarchical TiO_2 nanorod spheres were immobilized onto glass slide thus reducing the photocatalytic activity as compared to a suspension state. In the suspension state, the function of hierarchical structured TiO_2 photocatalysts can be maximized, due to the sufficient contact between catalysts, pollutants and the irradiated light (Molinari et al. 2002). Therefore, this shows the challenges during the synthesis of hierarchical TiO_2 nanorod spheres without the assistance of substrate or other similar templates.

2.6.3. Resorcinol and Formaldehyde Reaction for the Synthesis of TiO_2

Spheres

Considering the many disadvantages in synthesizing hierarchical TiO_2 nanorod spheres such as low productivity, easy aggregation, poor crystallization, it is imperative to develop a novel synthesis route to overcome these issues in order to broaden the application of hierarchical TiO_2 nanorod spheres in the clean water and energy generation on large scale.

Stöber et al. (1968) developed the Stöber method to control the growth of monodisperse spherical silica particles of uniform size through the hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions. Using the Stöber method, Liu et al. (2011d) was able to achieve excellent control of particle size, narrowed size distribution, smooth, spherical morphology of the resulting silica, microporous silica, and mesoporous silica particles.

Leveraging on the hydrolysis polymerization reaction mechanism of silicate sol-gel process in the Stöber method, Pekala et al., reported the use of resorcinol/formaldehyde in an analogous base-catalyzed aqueous polycondensation process to fabricate RF aerogels (Lu et al. 1992). In this polymerization process, resorcinol serves as a trifunctional monomer capable of adding formaldehyde in the 2-, 4- and 6- ring positions. This monomer is especially reactive due to its attached hydroxyl groups. The substituted resorcinol rings agglomerate to form clusters of 3 to 20 nm in the solution. The cluster size is regulated by the concentration of catalyst. These clusters have surface groups, such as $-\text{CH}_2\text{OH}$, that react further to form a dark red gel (Lu et al. 1992, Pekala 1989).

Since then, the resorcinol-formaldehyde reaction has been widely studied in the preparation of organic and carbon gels with unique structural features and performance characteristics. The resulting nanostructure was very sensitive to various

synthesis and process conditions, which lead to its remarkable potential for designing and tailoring materials to fit specific synthetic conditions for novel material fabrications (Al-Muhtaseb and Ritter 2003). Although the silica spheres and RF spheres have been successfully fabricated, it is still not easy to prepare inorganic spheres with the Stöber or RF method.

Only few have reported the successful fabrication of TiO_2 based nanoparticles or spheres using the sol-gel polycondensation of resorcinol with formaldehyde. In Neti et al. (2010) study, C-doped TiO_2 nanoparticles were synthesized from a sol-gel polycondensation of resorcinol with formaldehyde with the addition of TTIP. The mesoporous TiO_2 fabricated was a result of spontaneous reaction between TTIP and RF gel, which resulted in rapid solidification of gel (Thovicha and Pavarajarn 2011). A TiO_2 -carbon aerogel (TiO_2/CA) prepared via copolymerization of tetrabutyl orthotitanate with resorcinol-formaldehyde solution was used in catalytic decomposition of isopropanol (Maldonado-Hòdar et al. 2000, Maldonado-Hòdar et al. 2000). Jin et al. (2011) showed that a TiO_2 /carbon aerogel (TiO_2/CA) electrode prepared from ambient drying and the resorcinol-formaldehyde method, displayed high electrosorption behaviors for degradation of high-concentration dye wastewater. We recently reported that the synthesis of hierarchical porous TiO_2 hollow microspheres using RF reaction with inorganic Ti precursor (TiCl_3), followed by high temperature calcination was the easiest method for scale up production of hierarchical porous TiO_2 hollow microspheres with excellent photocatalytic activity for water purification (Liu et al. 2011c).

2.7. Simultaneous Water Purification and Clean Energy Generation in a Heterogeneous Photocatalytic System

The TiO₂ photocatalytic water splitting for H₂ generation has two challenges (Kudo and Miseki 2009, Ni et al. 2007). First the generated H₂ and O₂ will readily undergo a reversible reaction back into H₂O, thus reducing the generation rate of H₂. Second the overall water splitting reaction is an uphill reaction, which is not easy to achieve it. To address the first challenge, a sacrificial reagent such as methanol is always used to scavenge the holes instead of the H₂O. The holes scavenger methanol will then be mineralized into H₂O and CO₂ consequently eliminating the reversible reaction of H₂ and O₂ into H₂O and promoting the generation of H₂. Similarly, when other organic pollutants in the wastewater are used as holes scavengers, it allows the simultaneous H₂ generation and clean water purification via degradation of organic pollutants in wastewater; in particular municipal wastewater which is rich with organic pollutants.

For example, powered and immobilized Pt/CdS/TiO₂ photocatalysts allows the simultaneous photocatalytic degradation of waste materials in aqueous solutions and H₂ production. The presence of CdS in the Pt/CdS/TiO₂ photocatalyst allows the utilization of solar light, where Pt facilitates the high efficiency H₂ generation (Daskalaki et al. 2010). In addition, Pt/TiO₂ in a suspension system was also reported to be able to simultaneously generate H₂ and eliminate azo-dyes (Patsoura et al. 2006). Furthermore the Pt/TiO₂ photocatalyst was also reported to be able to simultaneously

generate H_2 and photodegrade a number of organic compounds including alcohols and organic acids (Patsoura et al. 2007).

It is ideal approach to synthesize high efficiency TiO_2 photocatalyst to promote the overall water splitting reaction. Metal doped TiO_2 photocatalyst proved to be able to improve the photocatalytic activity of TiO_2 for overall water splitting. Metals such as Pt doped on the surface of TiO_2 acts as active sites for H_2 generation. Recently, Cu doped TiO_2 photocatalysts were found to be able to enhance the photocatalytic H_2 generation activity (Xu et al. 2011). Moreover, copper is an abundant and inexpensive metal therefore it is considered to be the most promising metal to be used for H_2 generation.

Due to rapid industrialization, it has resulted in the generation of severely polluted water, particularly from the electroplating industry which generates wastewater rich with Cu^{2+} (Foster et al. 1993). It has become a huge challenge to recover Cu^{2+} from wastewater to allow it to be recycled. Researchers reported that it is possible to simultaneously recover Cu^{2+} and generate H_2 in a TiO_2 photocatalytic system. In this system, Cu^{2+} will be photocatalytically reduced into metal Cu before it deposits on the surface of TiO_2 . This deposited metal Cu then acts as active sites for photocatalytic H_2 generation (Troupis et al. 2002). This process shows the capabilities of heterogeneous photocatalytic system to simultaneously recover Cu^{2+} and generate H_2 (Xu et al. 2011).

Considering the above-mentioned analysis, it is ideal to simultaneously generate clean energy and purify wastewater in a photocatalytic system. Therefore it is imperative to synthesize high efficiency TiO_2 photocatalyst, which will be a centre of our study.

2.8. Summary

Through broad literatures reviews, it can be found that a low-temperature hydrothermal method to synthesize hierarchical TiO_2 nanorod spheres is a good approach. This developed hydrothermal method is able to synthesize hierarchical TiO_2 nanorod spheres without the assistance of template. However, the hydrothermal method has low reproductive ability and low production rate. It is also not favorable for formation of well crystallized TiO_2 and exposure of highly reactive facets, which are the limiting factors for high photocatalytic activity. Taking all the above-mentioned disadvantages into accounts, a novel high temperature calcination method can be used through deliberately adding TiCl_3 into the resorcinol and formaldehyde reaction. High temperature calcination method would result in good crystallization of TiO_2 and is easy for reproduction on large scale. Furthermore, the hierarchical TiO_2 nanorod sphere has a large percentage exposure of highly reactive facets which is imperative to the improvement of photocatalytic activity. To the best of my knowledge, this is the first time hierarchical TiO_2 nanorod spheres are synthesized using a high temperature calcination method.

CHAPTER 3 METHODOLOGY

3.1. Introduction

This Chapter provides an overview of all the experimental details for the basis of the findings of this study. First, the materials and methods used for synthesis of hierarchical TiO₂ nanorod spheres will be explained. Thereafter the characterization techniques used for studying hierarchical TiO₂ nanorod spheres will be covered. Finally, the methods used for investigating the photocatalytic activity of hierarchical TiO₂ nanorod spheres will also be introduced.

3.2. Chemicals

Tetra-n-butylorthotitanate [Ti(OC₄H₉)₄](TBOT)

Contains $\geq 98\%$ Ti(OC₄H₉)₄, purchased from Merck, Germany.

Titanium Trichloride (TiCl₃)

20 % content of TiCl₃ in 3 % HCl solution, obtained from Merck, Germany was used as the precursor for the preparation of hierarchical TiO₂ nanorod spheres using low temperature hydrothermal method and high temperature calcination method.

Resorcinol

Obtained from Merck, Germany was used to prepare the hydro gel solution for the fabrication of hierarchical TiO₂ nanorod spheres using high temperature calcination method.

Formaldehyde

Purchased from Merck, was used for the formation of hydro gel solution for the fabrication of hierarchical TiO₂ nanorod spheres using high temperature calcination method.

Deionized (DI) Ultra Pure Water

Millipore ultra pure water machine was used to produce ultra pure water for this study. Ultrapure water Milli-Q water: 18.2 MΩ.cm@25 °C, TOC<10 ppb.

Sodium Hydroxide (NaOH)

Obtained from Merck, Germany and was used to adjust pH value of the precursor for the synthesis of hierarchical TiO₂ nanorod spheres using low temperature hydrothermal method.

Hydrochloric Acid (HCl)

Analytical grade HCl, obtained from APS AJAX Finechem, Australia, and was used to adjust pH value of the precursor for the synthesis of hierarchical TiO₂ nanorod spheres using low temperature hydrothermal method.

3.3. Materials Synthesis

3.3.1. Hydrothermal Synthesis of Hierarchical TiO₂ Nanorod Spheres

2.5 mL TiCl₃ was readily dissolved in 27.5 mL saturated NaCl solution. The pH value of the mixed solution was adjusted to 3 with NaOH solution, subsequently the mixture was filled into a 40 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an electrical oven at 190 °C for 3 hours.

The autoclave was naturally cooled down in air, before it was opened. The clear supernatant was poured away and the white precipitates, synthesized TiO₂ nanorod spheres were transferred into a centrifugation tube. TiO₂ nanorod spheres were repeatedly washed with DI water and dried for further characterization and usage.

3.3.2. Hierarchical TiO₂ Nanorod Spheres Synthesized by High Temperature

Calcination

In a typical synthesis procedure, a 250 mL water flask was fixed in a water bath under stirring. Thereafter, 20 mL DI water was added into the flask, next 50 mL TiCl₃ aqueous solution (1.5 mol/L), resorcinol (R) (0.5 mol/L) and 6 mL formaldehyde (F) solution (35 wt %) was continuously added into the flask (Liu et al. 2011c, Friedel and Greulich-Weber 2006). Under continuous heating and stirring, the well-mixed solution was allowed to react at 90 °C for 2 hours to form the crescent Ti/RF spheres. After drying naturally, the crescent Ti/RF spheres were calcined in the furnace at 500 °C for 2 hours to obtain the final products. In order to evaluate the effects of different calcination temperature and atmosphere on the morphology evolution of hierarchical TiO₂ nanorod spheres and its photocatalytic activity, the crescent Ti/RF spheres were calcined under different atmospheres (air and N₂) and temperatures ranging from 400 °C to 900 °C.

In the polymerization process, resorcinol and formaldehyde cross-linked together forming the RF spheres as shown in Figure 3.1. The Ti³⁺ reacted with oxygen in the solution forming TiO₂ and grew along [001] direction with Cl⁻ acting as a

crystallographic controlling agent. Then TiO_2 nanorods were *in-situ* wrapped up by RF spheres forming crescent Ti/RF spheres as shown in Figure 3.1a (Figure 3.1c is the corresponding bulk photo). In the crystallization process, residual organics were burned off, then the TiO_2 nanorod spheres formed as shown in Figure 3.1b (Figure 3.1d is the corresponding bulk photo, from which the TiO_2 nanorod spheres appeared to be light yellow).

Figure 3.1 The formation route of TiO_2 nanorod spheres

3.3.3. Calcination under Atmospheric and N_2 Condition

The crescent Ti/RF spheres formed in the polymerization process were calcined under different atmospheres (air and N_2 condition) at different temperatures. The calcined products were characterized and investigated for photocatalytic water purification and H_2 generation under the irradiation of UV light.

3.4. Materials Characterization

3.4.1. Scanning Electron Microscopy (SEM)

Here, one scanning electron microscopy (SEM, EVO 56 Carl Zesis) was used to observe the morphology of the synthesized samples at the beginning stage. This is a normal SEM with a relative low resolution.

3.4.2. Field Emission Scanning Electron Microscopy (FESEM)

Two kinds of field emission scanning electron microscopy (FESEM, Jeol JSM-6340F and JSM-7600F) were used to observe the morphologies of samples. The Jeol JSM-6340F is an older model which allows good resolution images to be taken. While the Jeol JSM-7600F is a newer model to be capable of taking ultrahigh resolution images using its thermal emitter. The detailed specifications of the field emission scanning electron microscopy are summarized in the below Table 3.1. The element composition of samples were measured by an energy dispersive detector (EDS) (Oxford, 80 mm²) attached to the FESEM (Jeol JSM-7600F). A scanning transmission electron microscopy (STEM) detector attached to the FESEM (JSM-7600F) was also used to observe the samples.

Table 3.1 Detailed descriptions of the different detectors attached in Jeol JSM-7600F

	Resolution	Observable information
In-Lens thermal FEG including upper detector and lower detector	High resolution <ul style="list-style-type: none"> • nm at 15 kV • 1.5 nm at 1 kV • 5.0 nm at 0.1 kV 	Topography and morphology information of the samples
Low Angle Backscattered Electron Detector (LABe)	Hi-resolution backscattered electron (BSE) imaging at low energies;	Composition information (heavy element appears brighter) at large working distance (>6 mm) Both composition information and topography information can be obtained at low working distance (<6 mm)
Scanning Transmission Electron Microscopy (STEM)	Resolution 0.8 nm at 30 kV	Two dimensional information of the specimens under dark or bright field; --Bright field: heavy element appears dark --Dark field: heavy element appears bright
Energy Dispersive Spectrometer (EDS) 80 mm² silicon drift detector	129 eV resolution	Quantitative and qualitative Composition information and the element mapping information of the specimens

3.4.3. Transmission Electron Microscopy (TEM)

The morphologies and the lattice fringe of TiO₂ nanorods were measured using the transmission electron microscopy (TEM, Jeol JEM-2010), with an accelerated voltage of 200 kV. Prior to measurement, the samples were dispersed in absolute ethanol solution under ultrasonication, before it was dipped in carbon coated Cu grid ready for TEM observation.

3.4.4. Crystal Phase Determination by XRD

The structure and crystal phase of hierarchical TiO₂ nanorod spheres were determined using powder X-ray diffractometer (XRD, Bruker AXS D8 advance) with

monochromated high-intensity Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) operated at 40 kV and 30 mA across a 2θ range of 10° to 80° .

3.4.5. Measurement of Chemical Composition and Electronic Structure by XPS

X-ray photoelectron spectrometer (XPS) (Kratos Axis Ultra Spectrometer) with a monochromic Al K α source at 1486.7 eV, at a voltage of 15 kV and an emission current of 10 mA was employed to measure the chemical composition and electron structures of hierarchical TiO₂ nanorod spheres. The carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (eV).

3.4.6. Light Absorption Capability Investigation of the Hierarchical TiO₂ Nanorod Spheres

The UV-Vis spectra of samples were obtained using a Thermo Scientific Evolution 300 UV-Vis spectrometer (Thermo Fisher Scientific, Massachusetts, USA) equipped with an integrating sphere assembly and a Xenon lamp source. BaSO₄ was used as the reflectance standard. The spectra were converted from reflectance to absorbance and the indirect bandgaps were obtained by the Kubelka-Munk transformation as follows.

$$\alpha = \frac{(1-R)^2}{2R} \quad \dots (1)$$

$$\alpha h\nu = C_1(h\nu - E_g)^2 \quad \dots (2)$$

$$h\nu = \frac{1240}{\lambda} \quad \dots (3)$$

Where,

α is optical absorption coefficient near the absorption edge for indirect interband transitions,

R is the reflectance of the semiconductor, $R=10^{-A}$ (A is an optical absorbance)

C_I is the absorption constant for an indirect transition,

$h\nu$ is photon energy,

E_g is the indirect bandgap energy (eV),

λ is the wavelength (nm).

3.4.7. Measurement of Porous Structure and Specific Surface Area by N₂

Adsorption/Desorption Method

The porous structures of hierarchical TiO₂ nanorod spheres were characterized by N₂ adsorption/desorption isotherms using a Micromeritics ASAP 2040 system at liquid nitrogen temperature (77 K). Before measurement, 0.1 g sample was out-gassed under vacuum for 6 hours at 250 °C. Pore volume and diameter distributions were derived from the desorption branches of the isotherms by the Barrett-Joyner-Halenda (BJH) model, and the Brunauer-Emmett-Teller (BET) specific surface areas were calculated from the linear portions of the BET plots.

3.4.8. Photoluminescence Analysis (PL)

Photoluminescence analysis was conducted using a Fluorolog-3 spectrofluorometer, equipped with a Nd:YAG laser system of excitation wavelength at 320 nm (Horiba Scientific, New Jersey, USA).

3.4.9. Thermal Gravimetric Analysis (TGA)

The thermal degradation and crystallization process of the crescent Ti/RF spheres were investigated under nitrogen purging conditions using Perkin Elmer TAG7 thermogravimetric analyzer, from room temperature (30 °C) to 900 °C, at a heating rate of 10 °C/min. The TGA analysis was conducted under both under N₂ gas and atmospheric conditions.

3.4.10. Gas Measurement

Gas produced via the photocatalytic reaction was analyzed using an off-line TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A).

3.4.11. Ion Concentration Measurement

The ion concentration of Cu²⁺ was quantified at stated time intervals by an inductively coupled plasma emission spectroscopy (ICP, Perkin Elmer Optima 2000DV).

3.5. Performance Evaluation of the Hierarchical TiO₂ Nanorod Spheres

The performance of hierarchical TiO₂ nanorod spheres under different conditions were evaluated by photocatalytic degrading several kinds of probe contaminants including Acid Orange 7 (AO 7), Rhodamine B (RhB), and Methylene blue (MB). At the same time, the hierarchical TiO₂ nanorod spheres synthesized by high temperature calcination were also applied for simultaneous Cu²⁺ recovery and photocatalytic H₂

generation under the irradiation of UV light. The detailed experimental procedures will be explained in the following sections.

3.5.1. Evaluation of Photocatalytic Activity

3.5.1.1. Photocatalytic Degradation of AO 7

As a common organic dye in wastewater, AO 7 was used as a probe contaminant to compare the photocatalytic activities of TiO₂ nanorod spheres and commercial TiO₂ P25 (Degussa). The photocatalytic activity was conducted in a cylinder reactor (100 mL), AO 7 solution with initial concentration of 50 mg/L (pH 7) and TiO₂ photocatalyst (50 mg/L) were mixed in the reactor continuously with a magnetic stirrer at bottom (Bai et al. 2010, 2011b). Then one UVP UV light (predominate wavelength at 254 nm) was suspended in the middle of cylinder reactor. After the adsorption equilibrium reached at 30 min, the UV light was switched on to start photocatalytic test. At different time intervals, 3 mL of reaction solution was withdrawn using a syringe to monitor its UV absorption spectra by a UV-visible photospectrometer. The photodegradation of AO 7 by commercial TiO₂ P25 was also conducted under the same conditions. The absorption spectra of AO 7 solution at different time after irradiation with UV light and with the presence of TiO₂ nanorod spheres were obtained, the kinetic degradation curve of AO 7 by TiO₂ nanorod spheres and TiO₂ P25 was then plotted.

3.5.1.2. Photocatalytic Degradation of RhB

Similar to AO 7, RhB was also used as a probe contaminant to investigate the photocatalytic activity of hierarchical TiO₂ nanorod spheres. The experimental procedure is as follows. A 100 mL cylinder was used as the reactor to hold the reaction solution. RhB with an initial concentration of 50 mg/L and TiO₂ photocatalyst (50 mg/L) was mixed in the reactor with a magnetic stirrer at bottom (Bai et al. 2010, 2011b). This mixed solution was kept in dark for 1 hour to obtain the adsorption equilibrium. Thereafter one UVP UV light (predominate wavelength at 254 nm) was suspended in the middle of cylinder reactor. The UV light was switched on to start photocatalytic test. At different time intervals, 3 mL reaction solution was withdrawn using a syringe and the UV absorption spectra was observed by employing a UV-visible photospectrometer. The absorption spectra of RhB solution at different time after irradiation with UV light were obtained, and the kinetic degradation curve of RhB by TiO₂ nanorod spheres was simulated by first-order degradation model, the kinetic degradation constant (k) was also recorded as an indicator to compare the activity of hierarchical TiO₂ nanorod spheres synthesized under different conditions.

3.5.1.3. Photocatalytic Degradation of MB

Like AO 7, a popularly used organic dye pollutant MB was also used as a probe contaminant to evaluate the photocatalytic activity of hierarchical TiO₂ nanorod spheres. The photocatalytic activity was conducted in a cylinder reactor (100 mL), MB solution with initial concentration of 50 mg/L (pH 7) and TiO₂ photocatalyst (50

mg/L) was mixed in the reactor with a magnetic stirrer at bottom (Bai et al. 2010, 2011b). Thereafter one UVP UV light (predominate wavelength at 254 nm) was suspended in the middle of cylinder reactor. After adsorption equilibrium reached at 30 min, the UV light was switched on to start photocatalytic test. At different time intervals, 3 mL reaction solution was withdrawn using a syringe and the UV absorption spectra was observed by employing a UV-visible photospectrometer. The photodegradation of MB by commercial TiO₂ P25 was also conducted under the same conditions.

During the photocatalytic test process, the Pall filter (pore size: 0.2 µm, diameter: 33 mm, hydrophilic polyethersulfone) was used to remove photocatalysts from the reacted solution before UV-absorption value was measured. A Semi-micro Cuvette (1.6 mL, PS, Greiner bio-one GmbH, Austria) was used for the tests of UV-vis absorption spectra by photospectrometer.

3.5.2. Evaluation of Photocatalytic H₂ Generation Activity

The photocatalytic reaction was performed in a self-designed inner-irradiation type Pyrex reactor (volume: 270 mL) equipped with a 400 W high pressure Hg lamp (Riko, UVL-400 HA) as light source. Figure 3.2 shows the schematic diagram of photocatalytic H₂ generation reactor. A constant reactor temperature of 25 °C was maintained with the use of a quartz water jacket, which was cooled by recycling water and was utilized to cover the lamp. Cu(NO₃)₂ was first dissolved in 10 volume % methanol/water mixture with Cu²⁺ concentration of 200 mg/L, and TiO₂ nanorod

spheres were then dispersed into the solution at a dosage of 1 g/L. Prior to irradiation, the reactor was purged thoroughly with Nitrogen gas for 30 min to de-aerate the reactor. The H₂ gas generated from photocatalytic reaction was collected by a water replacement trap and was analyzed using a TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A).

Figure 3.2 Schematic diagram of the suspended system of H₂ generation reactor setup (Lee et al. 2012)

3.6. Summary

In this chapter, the materials and methods used were introduced. First, the detailed information for all the materials such as the brands, compositions, purities was introduced. Second, the approach used to synthesize the hierarchical TiO₂ nanorod spheres using low temperature hydrothermal method and the novel developed high

temperature calcination through deliberately adding TiCl_3 into the resorcinol and formaldehyde reaction was explained. Third, the variety of analytical techniques and equipment applied for characterizing the hierarchical TiO_2 nanorod spheres so as to reveal its formation mechanism were systematically introduced. Finally, the testing procedure for evaluating the performance of hierarchical TiO_2 nanorod spheres was also described in this chapter.

CHAPTER 4 FACILE LOW TEMPERATURE HYDROTHERMAL SYNTHESIS OF HIERARCHICAL TiO₂ NANOROD SPHERES

4.1. Introduction

As discussed in Chapter 2, owing to its unique properties such as environmental benign, low cost, chemical stability, large surface area, easy for reuse, enhanced light absorption capability and high photocatalytic activity, hierarchical TiO₂ nanorod spheres has attracted considerable attentions. Hence, the objective of this Chapter is to develop a facile low-temperature hydrothermal method to synthesize hierarchical TiO₂ nanorod spheres without the assistance of template for concurrent photocatalysis and membrane filtration water purification. This breakthrough will help to overcome the restrictions of use of a template and to promote the development of low-temperature hydrothermal method for the synthesis of TiO₂ nanorod spheres.

In this chapter, the results from the series of characterizations and the concurrent photocatalytic membrane filtration system will be discussed.

4.2. Characterization

The morphology of TiO₂ nanorod spheres was observed by FESEM. As shown in Figure 4.1, TiO₂ nanorod spheres have been successfully synthesized by low-

temperature hydrothermal method. Figure 4.1a depicted the image of several TiO₂ nanorod spheres with uniform dimensions. While Figure 4.1b showed an individual TiO₂ nanorod sphere with the sizes ranging from 1 to 2 μm . The length and outer diameter of TiO₂ nanorods and their comprising spheres are between 500 nm to 1 μm and tens of nanometer, respectively. Figure 4.1c was an enlarged image of Figure 4.1b to highlight the outwardly growing TiO₂ nanorods. In Figure 4.1b, it showed that TiO₂ nanorods nucleated from the core and gradually grew outwards eventually forming an entire sphere.

The hierarchical characteristics of TiO₂ nanorod spheres were also revealed by Figure 4.1a, in which: the distance between different TiO₂ nanorod spheres are in the range of micrometer scale, while the distance between different TiO₂ nanorods are in the range of nanometer scale. The hierarchical property of TiO₂ nanorod spheres is beneficial for the improvement of photocatalytic activity in terms of (1) its enlarged specific surface area to allow fast mass transfer and to provide more reaction sites, (2) the improved light absorption capability by allowing more light reflection and multiple scattering inside interiors, and (3) the retardation of recombination of photogenerated electrons and holes by promoting electrons transfer along 1D TiO₂ nanorods (Fonzo et al. 2009).

Figure 4.1 FESEM images of the hierarchical TiO_2 nanorod spheres, (a) several TiO_2 nanorod spheres, (b) an individual TiO_2 nanorod sphere, (c) enlarged image of the individual TiO_2 nanorod sphere in (b), and (d) the core part of the TiO_2 nanorod sphere

TEM was employed to observe the morphology of TiO_2 nanorod spheres as shown in Figure 4.2. From Figure 4.2a, it provides evidence that TiO_2 nanorods nucleated from the core and grew outwards eventually forming an entire sphere. The enlarged image in Figure 4.2b illustrates the dimensions of TiO_2 nanorod, which were similar to the images observed by FESEM.

Figure 4.2 TEM images of TiO₂ nanorod spheres, (a) overall image of the several TiO₂ nanorod spheres, and (b) enlarged image of the rectangular selected area of TiO₂ nanorod sphere in (a) showing that TiO₂ nanorod growing outwardly

The crystal phase of TiO₂ nanorod spheres were determined by XRD as shown in Figure 4.3. The TiO₂ nanorod spheres were crystallized into a rutile structure (JCPDS 89-0552). This is in accordance with the previous reports (Feng et al. 2005, Liu et al. 2007c, Ribeiro et al. 2007, Wang et al. 2009). This formation could be attributed to the strong acidic condition which is favorable for the formation of rutile TiO₂ (Cheng et al. 1995). Furthermore, the stronger (110) peak from XRD pattern were in contrast to standard rutile peak reflects that the TiO₂ nanorods had a preferred growing orientation as a result of the Cl⁻ in the reaction solution (Filankembo et al. 2003). From the FESEM, TEM and XRD pattern, it can be concluded that the formation mechanism of TiO₂ nanorod spheres is as follows: (1) Ti³⁺ slowly released from the hydrolysis of TiCl₃ and then was oxidized into rutile TiO₂ under acidic condition, (2) the TiO₂ slowly formed and grew along the preferred orientation with the influence of Cl⁻ in the reaction solution, and (3) the growing TiO₂ nanorods self-assembled into spheres. The growth of TiO₂ nanorods due to the presence of adsorbed Cl⁻ on the (110)

plane of rutile TiO₂ which suppresses and accelerates the growth of TiO₂ along [110] and [001] direction, respectively (Hosono et al. 2004).

Figure 4.3 XRD pattern of the TiO₂ nanorod spheres

The elemental compositions of TiO₂ nanorod spheres were investigated by EDS spectrum in Figure 4.4 with detailed elemental contents listed in Table 4.1. Clearly the element of Ti and O dominate the components of TiO₂ nanorod spheres, no other impurities were detected. The atomic ratio of Ti: O revealed by Table 4.1 was not in accordance to its stoichiometry (Ti: O = 1:2). This could be a result from adsorption of the additional Ti on the surface of TiO₂ nanorod spheres that were not removed during post treatment process.

Table 4.1 Element contents of TiO₂ nanorod spheres corresponding to EDS spectrum

	keV	Mass %	Atom %
C K	0.277	2.42	1.4198
O K	0.525	25.44	10.0081
Ti K	4.508	69.71	86.2975
Au K	2.121	2.43	2.2746
Total		100	100

Figure 4.4 EDS spectrum of TiO₂ nanorod spheres

Figure 4.5 N₂ adsorption/desorption isotherm curve of the TiO₂ nanorod spheres

The porous structure of TiO₂ nanorod spheres were analyzed using the N₂ adsorption/desorption isotherm curve in Figure 4.5. The plot shows that TiO₂ nanorod spheres possess the property of mesoporous materials due to the distance between the nanorods. This provides evidence of its hierarchical characteristic with multi-scaled organizations. The BJH pore size distribution of TiO₂ nanorod spheres were shown in Figure 4.6. Two dominant peaks were observed at around 3 nm and 10 nm, which can be ascribed to the distances between TiO₂ nanorods at different positions. The peak at 3 nm is postulated to be the distance between TiO₂ nanorods to the core of sphere, while the latter peak at 10 nm is ascribed to the distance between TiO₂ nanorods to the outward end of sphere, which is in accordance to the FESEM and TEM observations. From the BET specific surface area analysis, TiO₂ nanorod spheres had a specific surface area of 44.73 m²/g, which is larger than that of commercial TiO₂ P25 (34.38 m²/g).

Figure 4.6 BJH pore size distribution of the TiO₂ nanorod spheres determined by N₂ desorption method

As shown in Figure 4.7, hierarchical structured TiO₂ nanorod spheres possess the enhanced light absorption capability. The hierarchical structured TiO₂ nanorod spheres underwent a redshift and displayed a stronger absorption in the visible range in a comparison to commercial TiO₂ P25. This improved absorption can be attributed to the micro/nano-scaled hierarchical structure of the TiO₂ nanorod spheres which allows more light reflection and multiple scattering within the interior (Pan et al. 2008, Zhao et al. 2008). Furthermore, the enlarged specific surface area of the TiO₂ nanorod spheres also improves its light harvesting ability (Zhou et al. 2010).

The diffusive reflectance measurements were converted into the equivalent absorption coefficient using the Kubelka-Munk function. As shown in Figure 4.7b, the TiO₂ nanorod spheres had narrower indirect bandgap (E_g) in a comparison to TiO₂ P25 due to the redshift of UV absorption edge. The narrowed bandgap and the redshift of the UV absorption edge are both positive improvements made to enhance the photocatalytic activity of the TiO₂ nanorod spheres.

Figure 4.7 (a) UV-Visible spectra of TiO_2 nanorod spheres and TiO_2 P25, and (b) their corresponding Kubelka-Munk functions

4.3. Concurrent Photocatalysis and Membrane Filtration for Water Purification

Figure 4.8 The apparatus diagram about the concurrent photocatalysis and membrane filtration system for water purification

A “win-win” strategy was developed for water purification using a concurrent photocatalysis and membrane filtration system. In this concurrent system, a novel multifunctional membrane was fabricated by assembling TiO₂ nanorod spheres on the surface of a polymer membrane using a dead-end filtration apparatus as shown in Figure 4.8. From the FESEM images in Figure 4.9, the novel porous functional layer formed by uniformly assembling hierarchical TiO₂ nanorod spheres on the surface of polymer membrane. This multifunctional membrane can then be used in photocatalytic degradation of pollutants. Under irradiation of UV light, this multifunctional membrane possess a self-cleaning mechanism which can mitigate membrane fouling thus allowing the production of high quality water at a constant

high flux. In order to examine the engineering application of the TiO₂ nanorod membrane, a ubiquitous pollutant (HA) found in the surface and ground water and an industrially dye (MB) were used as the probe pollutants in the concurrent photocatalytic degradation and membrane filtration set up. To establish a basis for comparison, the TiO₂ P25 membranes were also assembled using the same approach.

Figure 4.9 FESEM images of TiO₂ nanorod membrane with a clear indication of the multi-scale hierarchical structure. Wherein, the nano-scale is referred to the distances between different TiO₂ nanorods, the micro-scale is referred to the distances between different spheres

Figure 4.10a and b illustrate the difference between the hierarchical TiO₂ nanorod membrane and TiO₂ P25 deposited membrane. From the schematic diagrams and their respective SEM images of the membrane surfaces, the TiO₂ nanorod spheres constructed a hierarchical and porous functional layer on the surface of membrane, however the TiO₂ P25 nanoparticles deposited densely on the surface of membrane.

Figure 4.10 (a) Schematic diagram of hierarchical TiO_2 nanorod membrane and its surface SEM image; (b) diagram of TiO_2 P25 deposited membrane and its surface SEM image

Figure 4.11a displays the removal rates of MB and HA by hierarchical TiO_2 nanorod membrane and TiO_2 P25 deposited membrane. Starting with an identical initial concentration of MB and the same exposure of UV light (30 min), the removal rate of MB by hierarchical TiO_2 nanorod membrane appear to be superior to TiO_2 P25 deposited membrane. However, the removal of HA appears to be similar for both hierarchical TiO_2 nanorod membrane and TiO_2 P25 deposited membrane (Figure 4.11b). This reveals that hierarchical TiO_2 nanorod membrane had a strong capability in mitigating membrane fouling under the irradiation of UV light.

Figure 4.11 Performance investigation, (a) MB and HA removal rates by hierarchical TiO₂ nanorod membrane and TiO₂ P25 deposited membrane, and (b) the first-order kinetic curves of photodegradation of HA by TiO₂ nanorod membrane and TiO₂ P25 deposited membrane

Besides the high photodegradation of MB and HA under the irradiation of UV light, the flux performance of hierarchical TiO₂ nanorod membrane and TiO₂ P25 deposited membrane were also investigated using the experiment set up shown in Figure 4.8. The relationships between permeate flux and transmembrane pressure (TMP) for hierarchical TiO₂ nanorod membrane and P25 deposited membrane is shown in Figure 4.12. From the plot, the permeate flux of hierarchical TiO₂ nanorod membrane is proportional to TMP with a well fitted regression line ($R^2=0.99$), however the P25 deposited membrane ($R^2=0.77$) was significantly different from hierarchical TiO₂ nanorod membrane. Referring to the SEM images in Figure 4.10, the surface of TiO₂

nanorod membrane is hierarchical and porous which favors a higher permeate flux (Figure 4.10a), but the surface of P25 deposited membrane is dense therefore reducing the permeate flux of membrane (Figure 4.10b).

Figure 4.12 Permeate flux of hierarchical TiO₂ nanorod membrane and TiO₂ P25 deposited membrane at different TMP

4.4. Summary

The hierarchical TiO₂ nanorod spheres were successfully synthesized by a facile low temperature hydrothermal method without the assistance of template. From the experimental findings, the strong acidic condition played an important role in the formation of rutile TiO₂. The acidic condition allowed the slow release of Ti³⁺ from the hydrolysis of TiCl₃ which will be oxidized into TiO₂ by oxygen. The growth of TiO₂ had grew along the [110] direction due to the presence of the influence of Cl⁻. The Cl⁻ adsorbed on the (110) plane of rutile TiO₂ suppressed and accelerated the growth of TiO₂ along [110] and [001] direction, respectively. Finally, the growing TiO₂ nanorods self-assembled into hierarchical TiO₂ nanorod spheres. From the SEM/TEM images, it was observed that the distances between the spheres are in the

range of micrometer scale and the distances between TiO₂ nanorods comprising of the spheres are in the nanometer scale.

A “*win-win*” strategy was developed for water purification in a concurrent photocatalysis and membrane filtration system to showcase the engineering capability of the TiO₂ nanorod spheres. Under irradiation of UV light, the novel hierarchical TiO₂ nanorod membrane exhibited stronger abilities in photodegrading MB and HA in a comparison to TiO₂ P25 deposited membrane. Moreover, the porous functional layer created by the hierarchical TiO₂ nanorod spheres allowed water to pass through thus improving its flux performance.

These findings are not only of great significance in the development of hydrothermal synthesis of hierarchical TiO₂ nanorod spheres without the assistance of template, but also of immense importance in the development of a “*win-win*” strategy used to purify wastewater with high quality at low costs and in an environmental-friendly manner.

CHAPTER 5 FACILE FABRICATION OF HIERARCHICAL TiO₂ NANOROD SPHERES THROUGH HIGH TEMPERATURE CALCINATION

5.1. Introduction

Although the hierarchical TiO₂ nanorod spheres using a low temperature hydrothermal method without the assistance of template were successfully synthesized and tested (Chapter 4), the potential for its applications in water purification and clean energy generation is still limited due to the major drawbacks of hydrothermal method.

The hydrothermal method has low reproducibility and low production rate of TiO₂ nanorod spheres. In addition, the low-temperature hydrothermal process does not readily produce well crystallized TiO₂ with good photocatalytic activity. Moreover, hydrothermal process may cause aggregation of the resultant TiO₂ nanorod spheres, which deteriorates the photocatalytic reactions. Hence, it is necessary to further develop methods to synthesize hierarchical TiO₂ nanorod spheres with high photocatalytic activity for water purification and clean energy generation without the mentioned drawbacks of hydrothermal method.

In this Chapter, we will exhibit the findings from the characterizations conducted using a variety of techniques. We report a novel calcination method to fabricate hierarchical TiO₂ nanorod spheres with high photocatalytic activity for water purification and clean energy generation. The revelation of formation mechanism of hierarchical TiO₂ nanorod spheres via high temperature calcination method will also be discussed.

5.2. Characterization of TiO₂ Nanorod Spheres

The formation of TiO₂ nanorod spheres occurs in two steps. The first step is the formation of crescent Ti/RF spheres which provides the foundation for the development of TiO₂ nanorod spheres. Second, the Ti/RF spheres undergo a high temperature calcination which promotes the formation of well crystallized TiO₂ nanorod spheres. Here, the resorcinol and formaldehyde would react into RF spheres acting as templates to ease the formation of Ti/RF spheres.

In order to understand this process a blank control experiment was conducted where the RF spheres were synthesized without addition of TiCl₃ (Friedel and Greulich-Weber 2006). The mixed solution, of resorcinol (0.5 mol/L) and formaldehyde (35 wt%, 6 mL) was continuously stirred and allowed to react at 90 °C for 2 hours. Thereafter, the prepared gel was dissolved in absolute ethanol solution and dipped in a copper grid for TEM observations.

Figure 5.1 TEM image of the RF spheres synthesized from resorcinol and formaldehyde without the addition of TiCl₃

Figure 5.1 shows the TEM images of the RF spheres at different magnifications, these RF spheres have diameters of approximately 1 μm and will act as the template to *in-situ* wrap up the growing TiO₂ nanorods into TiO₂ nanorod spheres.

The FESEM and TEM images in Figure 5.2 depict the evolution routes of TiO₂ nanorod spheres. Beginning with Figures 5.2a – 5.2c, the series of images show the crescent Ti/RF spheres before calcination. Figure 5.2a clearly shows the presence of TiO₂ nanorods on the surface of crescent spheres (Figure 5.2b). Furthermore, the TEM image (Figure 5.2c) reveals that the crescent spheres were wrapping up the TiO₂ nanorods. By analyzing the FESEM and TEM images (Figures 5.2d – 5.2f) after TiO₂ nanorods spheres underwent calcination, several deductions could be made. The Figures 5.2d and Figure 5.2e provide evidence that RF spheres were burnt off during calcination process leaving the TiO₂ nanorods fully exposed. As illustrated in Figure 5.2f, each TiO₂ nanorod sphere had a well-defined spherical structure with an average

diameter of 1-2 μm and the length of the TiO₂ nanorods were approximately 500 nm. Furthermore, the FESEM images in Figure 5.2g and Figure 5.2h substantiate the existence of monodisperse TiO₂ nanorod spheres (Zhang et al. 2010).

Figure 5.2 FESEM and TEM images showing the evolution routes of the TiO₂ nanorod spheres. (a) SEM image of TiO₂ nanorod spheres before calcination, (b) enlarged SEM image of (a) reveals the tips of the TiO₂ nanorods on the surface of the sphere, (c) TEM image of the TiO₂ nanorod sphere before calcination, (d) SEM image of TiO₂ nanorod sphere after calcination, (e) enlarged SEM image of (d) revealing the individual TiO₂ nanorods in the sphere, (f) TEM image of the TiO₂ nanorod sphere after calcination, and (g)-(h) FESEM of monodisperse TiO₂ nanorod spheres after calcination

Therefore, using the calcination method to synthesize TiO₂ nanorod spheres, it eliminates the aggregation of TiO₂ nanorod spheres. Additionally, the synthesized TiO₂ nanorod spheres had hierarchical characteristics which will improve the photocatalytic activity of it.

Figure 5.3 XRD patterns of the TiO₂ nanorod spheres before and after calcination

The crystal phases of the TiO₂ nanorod spheres before and after calcination were determined by XRD patterns as shown in Figure 5.3. From the pattern, the diffraction peaks of the calcined TiO₂ nanorod spheres match well with the standard tetragonal rutile crystal structure of TiO₂ phase (space group $P4_2/mnm$; JCPDS file no. 21-1276) (Feng et al. 2005). Meanwhile, a weak diffraction peak was observed for the TiO₂ nanorod spheres before calcination. The presence of the diffraction peak can be attributed to the initial formation of rutile TiO₂ nanorods which were consistent with the observation by FESEM. The formation of rutile TiO₂ was ascribed to the acidic

condition of precursor solution (Cheng et al. 1995). However in contrast to the standard XRD pattern, an enhanced peak for the (110) reflection and a relatively low diffraction intensity for (101) and (111), indicates that the growth of TiO₂ nanorods has a preferred orientation (Feng et al. 2005). The growth of TiO₂ in the preferred orientation is caused by the adsorbed Cl⁻ on the (110) plane of rutile TiO₂ which suppressed and accelerated the growth along the [110] and [001] direction, respectively (Hosono et al. 2004). This phenomenon was similar to the reaction occurring in hydrothermal process.

Moreover, the XRD patterns in Figure 5.3 clearly reveals that the poorly crystallized rutile TiO₂ nanorods had formed in the crescent Ti/RF spheres before calcination. Thus it can be deduced that the calcination process has two key functions: (1) to burn off RF, and (2) to promote the crystallization of TiO₂ nanorod spheres. The formation of well-crystallized TiO₂ nanorod spheres is beneficial for the improvement of its photocatalytic activity (Liu et al. 2011c).

Figure 5.4 (a) FESEM image of TiO_2 nanorod sphere, (b) SEM-STEM image of TiO_2 nanorod sphere, (c) SAED pattern of TiO_2 nanorod, (d) typical HRTEM image of an individual TiO_2 nanorod, (e) HRTEM image of the selected rectangular area from the TiO_2 nanorod of (e), and (f) FESEM image of the TiO_2 nanorods showing the topography information

The enlarged FESEM image of TiO_2 nanorod sphere shown in Figure 5.4a indicated the uniform distribution of TiO_2 nanorods, its corresponding FESEM-STEM image of the edge of TiO_2 nanorod sphere was also revealed in Figure 5.4b. Furthermore, from these images it can be seen that TiO_2 nanorods uniformly grew inside the sphere at mean distance of 10 nm between two nearby nanorods. From the selected area electron diffraction (SAED) pattern in Figure 5.4c, it confirmed that each TiO_2 nanorod possesses single-crystal characteristics (Liu and Aydil 2009).

The HRTEM images in Figure 5.3d and Figure 5.3e shows that the TiO₂ nanorods grew along (001) orientation and the (110) atomic plane is perpendicular to the rod axis with a lattice spacing of 3.25 Å (Feng et al. 2005, Liu and Aydil 2009). The surface topography of TiO₂ nanorods is shown by the FESEM image in Figure 5.4f. From the FESEM image, the TiO₂ nanorod has a polyhedral morphology with a trapezoidal surface with a surface width of 100-200 nm. Moreover, the FESEM images shows that the top surface of the nanorod has the (001) facet, while the circumferential facets are the (110) facets, which accounts for about 95 % of the total energy reactive surfaces (Pan et al. 2011, Chen et al. 2010b). Such high percentage of exposed (110) facets is favorable for high photocatalytic activity (Bae and Ohno 2009, Ke et al. 2009).

Figure 5.5 EDS spectrum of the TiO₂ nanorod spheres

Table 5.1 Detailed element content of the TiO₂ nanorod spheres

Element	Mass %	Atom %
O K	39.45	66.11
Ti K	60.55	33.89
Total	100	100

The elemental composition of TiO₂ nanorod spheres were revealed by the EDS spectrum in Figure 5.5, and the corresponding element contents were listed in Table 5.1. Evidently, the element Ti and O dominate the composition of TiO₂ nanorod spheres with a Ti and O ratio consistent to its stoichiometry, which was different from the results obtained from the hydrothermally synthesized TiO₂ nanorod spheres.

The surface chemical composition and electronic structure of TiO₂ nanorod spheres were investigated using XPS analysis. The results from XPS survey spectra presented in Figure 5.6a confirmed the existence of Ti, O and C in TiO₂ nanorod spheres. The high resolution Ti 2p spectra (Figure 5.6b) exhibited two typical peaks corresponding to binding energies of 458.005 eV (Ti 2p_{3/2}) and 463.762 eV (Ti 2p_{1/2}) revealing that the oxidation state of Ti was +4 in the form of TiO₂ in the TiO₂ nanorod spheres. While, high resolution O 1s spectra (Figure 5.6c) shows two small peaks centered at around 529.16 eV and 530.812 eV. The former peak was ascribed to inherent to O atoms bound to metals (Ti⁴⁺-O) (Ng et al. 2010), while the latter peak indicated the possible surface contamination by hydroxyl species (Ng et al. 2010). The C 1s spectra (Figure 5.6d) can be de-convoluted into three peaks with binding energies of 284.6 eV, 286.132 eV and 288.447 eV. The peak at 284.6 eV was ascribed to the signal

from adventitious elements carbon which is inevitable in XPS measurement (Bai et al. 2011b), while the peak at 286.132 eV and 288.447 eV can be assigned to the formation of carbonate species (Li et al. 2005, Ren et al. 2007). The peak at 288.447 eV can be ascribed to Ti-O-C structure in carbon doped titania by substituting some of the lattice titanium atoms by carbon (Xiao and Ouyang 2009). Due to this carbon doping, the resultant TiO₂ nanorod spheres appear yellow (Figure 3.1). These carbon doped TiO₂ can improve the light absorption capability and adsorption of organic molecules by TiO₂ (Xu et al. 2010b, Yun et al. 2010). Additionally, the good conductivity of carbon would favor the charge transfer from bulk of TiO₂ thus inducing the desirable oxidation reactions (Xu et al. 2010b, Hahn et al. 2009).

Figure 5.6 (a) XPS survey spectra, and high resolution XPS spectrum of (b) Ti 2p, (c) O 1s and (d) C 1s of the TiO₂ nanorod spheres

The porous structure of TiO₂ nanorod spheres was examined using N₂ adsorption/desorption method (Bai et al. 2011b). The isotherm curve in Figure 5.7a clearly shows that the TiO₂ nanorod spheres exhibited typical mesoporous property. The BJH pore size distribution curve shown in the Figure 5.7b reveals that the distance between different TiO₂ nanorods within spheres are approximately 10 nm, which is in line with the observation made from the FESEM analysis in Figure 5.2. The BET specific surface area of TiO₂ nanorod spheres measured, with a value of 64.19 m²/g, which is significantly higher than commercial TiO₂ P25 (34.38 m²/g) (Bai et al. 2010).

Figure 5.7 (a) N₂ adsorption/desorption isotherm curve of TiO₂ nanorod spheres, and (b) its corresponding BJH pore size distribution determined by N₂ desorption method

As we have mentioned, hierarchical TiO₂ nanorod spheres possess the ability to red shift the light absorption edge from UV to visible range (Bai et al. 2010). With the successful doping of carbon, it is also favorable for redshifting the absorption edge to visible range (Wu et al. 2009). The light absorption ability of TiO₂ nanorod spheres were investigated using a UV-visible photospectrometer with TiO₂ P25 as reference. The absorption spectra plotted in Figure 5.8a indicates that TiO₂ nanorod spheres

demonstrated better light absorption ability than TiO₂ P25, due to its hierarchical structure which allows more light reflection and multiple scattering inside interior, and the presence of carbon doped on the surface of TiO₂ (Bai et al. 2010, Pan et al. 2008). Using the Kubelka-Munk function (Liu et al. 2007d) to convert diffusive reflectance measurements into the equivalent absorption coefficient, the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ was shown in the Figure 5.8b. The indirect bandgap (E_g) values of TiO₂ nanorod spheres and TiO₂ P25 were obtained to be 3.01 eV and 3.15 eV, respectively (Liu et al. 2007d). Evidently, the TiO₂ nanorod spheres had a narrower indirect bandgap than TiO₂ P25.

Figure 5.8 (a) UV-visible spectra of TiO₂ nanorod spheres in a comparison to TiO₂ P25, and (b) their corresponding Kubelka-Munk functions

5.3. Formation Mechanism Revelation

5.3.1. Unrevealed Mechanism behind the Formation of TiO₂ Nanorod Spheres

The detailed processes for the synthesis of monodisperse hierarchical TiO₂ nanorod spheres have been explained in Chapter 3. To the best of our knowledge, this is the first time hierarchical TiO₂ nanorod spheres were synthesized using a calcination

method. Hence, it is necessary to study the reaction mechanism that occurred during the synthesis process.

Referring to the schematic diagram in Figure 5.9, the major task of this section is to explain the reaction mechanism in the calcination process. From the literature reviews, the calcination temperature and atmosphere can significantly affect the final products. In order to investigate the effects of these phenomena; the TiO₂ nanorod spheres underwent calcinations at different temperatures and atmospheres. The detailed analysis of will be discussed in Chapter 6.

Figure 5.9 A schematic diagram showing the basic synthetic processes, in which, the black boxes indicated the unrevealed formation mechanisms

5.3.2. TGA Analysis

To understand the reaction mechanism that occurred during the calcination process, TGA was conducted to investigate the weight loss of the crescent Ti/RF spheres under N₂ and atmospheric conditions across a temperature range from 30 °C to 900 °C. From TGA profiles shown in the Figure 5.10, two different kinds of samples were prepared. The first sample, a wet sample refers to the crescent Ti/RF spheres formed after polymerization at 90 °C for 2 hours. The second sample, a dry sample refers to the crescent Ti/RF spheres formed after polymerization at 90 °C for 2 hours and were subsequently dried in an electronic oven at 105 °C for 2 hours. Evidently, the calcination atmosphere resulted in different weight losses of crescent Ti/RF spheres due to the different reactions occurring during the calcination process. Calcination under atmospheric condition would burn off RF spheres leaving behind the TiO₂; therefore the reduction in the mass can be attributed to the loss of C, H, Cl, and partial O during the calcinations process. However when the Ti/RF spheres was calcined under N₂ condition, it leads to the carbonization of C and the crystallization of TiO₂, hence the weight loss was only due to the loss of Cl, H and partial O. By observing the morphology and composition of the final products after calcination under N₂ condition, it leads to the formation of TiO₂ spheres and carbon spheres.

Figure 5.10 TGA graphs of the well-formed crescent Ti/RF spheres analyzed under atmospheric or N₂ conditions

In order to verify the above postulations, the weight loss of crescent Ti/RF spheres were theoretically calculated starting from the initial reactants. The comparison between the theoretical weight losses and the measured weight loss is summarized in Table 5.2. From the calculations, the theoretically calculated weight loss from the initial reactants was equal to the actual loss measured by TGA.

Table 5.2 Summary of detailed theoretical weight losses of crescent Ti/RF spheres after calcination under N₂ and atmospheric conditions in a comparison with that measured by TGA

Element	Weight (g)	%	TiO ₂ nanorod spheres calcined under N ₂ condition			TiO ₂ nanorod spheres calcined under O ₂ condition		
			Theoretical loss, %	Actual loss, %		Theoretical loss, %	Actual loss, %	
				Wet ^c	Dry ^d		Wet ^c	Dry ^d
Ti	1.55	10.96	-			-		
C	4.36	30.80	-			30.80		
Cl	4.17	29.47	29.47			29.47		
O (TiO ₂) ^a	1.03	7.31	-			-		
O (excess) ^b	3.03	21.43	21.43			21.43		
Total	14.16	100	50.91	58.92	35.81	81.72	82.98	63.43

Note: ^a the O in the TiO₂ calculated according to the Stoichiometric numbers of 1:2 (Ti: O) in TiO₂; ^b the excess oxygen excluded the part in TiO₂, equal to the total oxygen from the reactants subtracted the oxygen in TiO₂; ^c wet sample refers to the crescent Ti/RF spheres after polymerization for 2 hours at 90 °C; and ^d dry sample refers to the crescent Ti/RF spheres after polymerization for 2 hour reaction at 90 °C, and then was dried in an electronic oven for 2 hours at 105 °C.

Figure 5.11 shows the different weight losses of crescent Ti/RF spheres by theoretical calculation and TGA analysis. For the dry sample analyzed under N₂ condition, the weight loss below 100 °C was due to the evaporation of water and HCl. The gradual decrease of weight from 100 °C to 373 °C was due to the complete loss of HCl. The weight loss between 373 °C to 900 °C should be ascribed to the loss of ClO_x, this process will result in the final formation of TiO₂ nanorod spheres and the carbonization of carbon spheres (Zhang et al. 2008b).

For the wet and dry sample analyzed under atmospheric condition, greater weight loss was observed than the samples analyzed under N₂ condition. When the temperature is below 100 °C, the weight loss was mainly due to the evaporation of water and partial HCl. The further weight loss between 100 °C to 350 °C was ascribed

to the loss of Cl in the form of ClO_x. About 30 % weight loss was observed between 350 °C to 450 °C, which resulted from the combustion of C as shown in the theoretical calculation. The difference in the weight loss for the wet and dry sample between the theoretical calculation and that measured by TGA was indicated in Figure 5.11. **A** and **C** indicates the increased weight losses of wet sample compared to the theoretical weight loss both under N₂ and atmospheric conditions, this is due to the presence of excess water in the fresh sample; **B** and **D** indicates the reduced weight losses of dry sample compared to the theoretical weight loss both under N₂ and atmospheric condition, this is because part of HCl and H₂O have been evaporated in the pre-drying process in oven at 105 °C.

Figure 5.11 Comparison of weight losses of the crescent Ti/RF spheres between theoretical calculations and TGA analysis

5.3.3. The Coexistence of TiO₂ Nanorod Spheres and Carbon Spheres

The remaining products of crescent Ti/RF spheres after calcination under N₂ condition were observed by FESEM. From the FESEM images in Figure 5.12a and

5.12c, it clearly shows that both hierarchical TiO₂ nanorod spheres and smooth carbon spheres were found in the scanning area. The topography and the elemental composition information revealed by the FESEM images under LBE mode (Figure 5.12b and d) showed that the hierarchical TiO₂ nanorod spheres in white had an obvious needle like structure, while the carbon spheres in black possess smooth surfaces. The uniform contrast except the white (TiO₂ nanorod spheres) and black (carbon spheres) color further indicates that there were no other element remaining after the calcination under N₂ condition. From Figure 5.12a and b, the monodisperse hierarchical TiO₂ nanorod spheres formed after calcination under N₂ condition were similar to that formed under atmospheric condition. Figure 5.12e shows an individual round carbon sphere surrounded by hierarchical TiO₂ nanorod spheres, while the FESEM image in Figure 5.12f depicts an individual hierarchical TiO₂ nanorod spheres which has the same morphology as the TiO₂ nanorod spheres calcined under atmospheric condition.

Figure 5.12 (a)-(d) FESEM images of the coexistence of hierarchical TiO_2 nanorod spheres and carbon spheres after calcination under N_2 condition, (a) and (c) were the SEI images, while (b) and (d) were the corresponding images under LBE mode, (e) FESEM image of an individual carbon sphere surrounded by hierarchical TiO_2 nanorod spheres, and (f) FESEM image of an individual TiO_2 nanorod sphere

Figure 5.13 (a)-(b) FESEM image of coexistence of hierarchical TiO_2 nanorod spheres and carbon spheres taken by SEI detector and EDS detector respectively, EDS element mapping images of (c) C, (d) O and (e) Ti of the corresponding area shown in (b), and (f) EDS spectrum of the coexistence of hierarchical TiO_2 nanorod spheres and carbon spheres after calcination under N_2 condition

A further step was used to consolidate these findings as above mentioned. From the EDS mapping, a typical coexistence of hierarchical TiO_2 nanorod spheres and carbon spheres was shown in Figure 5.13a and 5.13b taken by SEI and EDS detector,

respectively. Comparing the difference between the element mapping images of C (Figure 5.13c), O (Figure 5.13d) and Ti (Figure 5.13e), the distribution of Ti, and O concentrated at the location of the TiO₂ nanorod spheres (circled in red) while C concentrated at carbon spheres shown in Figure 5.13b. This clearly proves that carbon spheres were formed from the carbonization of crescent Ti/RF spheres under N₂ condition. The EDS spectrum in Figure 5.13e further revealed that the Ti, O and C dominated the composition of the final products of the crescent Ti/RF spheres after calcination under N₂ condition and no other elements were present. This verifies that all other elements were completely burned off in the calcination process under N₂ purging which substantiates our previous explanations.

5.3.4. Revelation of the Formation Mechanism

Now the reaction pathways occurred during the calcination process of crescent Ti/RF spheres under atmospheric and N₂ condition can be revealed as below.

Under N₂ condition:

(Carbonization)

Under atmospheric condition:

(Combustion)

These reactions which occurred during the polymerization process for the synthesis of crescent Ti/RF spheres are similar to the hydrothermal process used to synthesize TiO₂ nanorod spheres. By combining the above proposed reaction pathways that occurred in the calcination process, the formation mechanism for the fabrication of hierarchical TiO₂ nanorod spheres by calcination method can be illustrated as shown in Figure 5.14.

Figure 5.14 The revelation of formation mechanism of the hierarchical TiO₂ nanorod spheres by the high temperature calcination method

5.4. Summary

In this Chapter, the findings from the characterizations conducted on the TiO₂ nanorod spheres synthesized through the novel calcinations method were discussed. The findings proved that this method is a breakthrough as it overcomes the limitation of the hydrothermal method in scale-up fabrication of monodisperse and well

crystallized single crystal hierarchical TiO₂ nanorod spheres with high photocatalytic activity for water purification and clean energy generation.

Furthermore, the formation mechanisms of the hierarchical TiO₂ nanorod spheres have been clearly revealed. The first step was the polymerization process, in which the growing rutile TiO₂ nanorods were *in-situ* wrapped up by the RF spheres into crescent Ti/RF spheres which was similar to a hydrothermal process. In addition, the strong acidic condition allows the formation of rutile TiO₂, moreover the presence of Cl⁻ induces the growing direction of TiO₂ along the [001] direction. The second calcination process was greatly related to the calcination atmosphere, which affects the type of reactions that will occur during the calcinations and consequently affecting the structural properties of the resultant products. The atmospheric condition only induced the formation of hierarchical TiO₂ nanorod spheres. Whereas the N₂ condition, not only induces the formation of the hierarchical TiO₂ nanorod spheres but also causes the carbonization of RF spheres into carbon spheres.

CHAPTE 6 EFFECT OF CALCINATION TEMPERATURE AND ATMOSPHERE ON HIERARCHICAL TIO₂ NANOROD SPHERES

6.1. Introduction

In the previous Chapter 5, we have analyzed the formation mechanism in the synthesis of TiO₂ nanorod spheres using a variety of characterization techniques. Both the calcination atmosphere and temperature play significant roles in the formation of hierarchical TiO₂ nanorod spheres, its structure, and its water purification and clean energy generation properties.

Thus, the experimental findings in this chapter were firstly used to study the effect of calcination atmosphere on the final products of crescent Ti/RF sphere. Second the effect of calcination temperature on the morphology evolution, crystallization, porous structure, light absorption capability, of the hierarchical TiO₂ nanorod spheres will be discussed. Third, the effect of the morphology evolution on the photocatalytic activity of hierarchical TiO₂ nanorod spheres for water purification and clean energy generation will also be investigated.

6.2. Hierarchical TiO₂ Nanorod Spheres Obtained after Calcination under Atmospheric Condition

Here, the effect of calcination temperature on the morphology evolution, crystallization, porous structure, UV-vis spectrum, BET specific surface area will be discussed. These factors play significant roles in the photocatalytic activity of hierarchical TiO₂ nanorod spheres. In order to clearly understand the effects, a series of well formed crescent Ti/RF spheres were calcined at various temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C) under atmospheric condition for 2 hours, respectively.

Herein, the TiO₂ nanorod spheres obtained after calcination will be designated as **TiO₂-T**, in which the “**T**” denotes the calcination temperature. For example, “**TiO₂-400**” indicates the TiO₂ nanorod spheres obtained after well formed crescent Ti/RF spheres which were calcined at 400 °C for 2 hours under atmospheric condition.

6.2.1. Effect of Calcination Temperature on Morphology Evolutions of Hierarchical TiO₂ Nanorod Spheres

Figure 6.1 FESEM images of well formed crescent Ti/RF spheres at different magnifications

The morphologies of crescent Ti/RF spheres are shown in Figure 6.1. From FESEM image, the crescent Ti/RF spheres were formed from the polymerization process of deliberately adding TiCl₃ into the resorcinol and formaldehyde reaction. Figures 6.1a and 6.1b show the overview image of crescent Ti/RF spheres, while Figures 6.1c and 6.1d display the high magnification images of individual Ti/RF sphere. The Ti/RF spheres were uniform and its circular structure was well defined. Furthermore observed from the high magnification FESEM images, thin flaky layers were seen attached on the surface of the individual sphere. The formation of this layer could be due to the presence of excess resorcinol and formaldehyde reactants which were

added. However the form of RF gels have yet to be determined as it is difficult to assess its form using the FESEM.

Figure 6.2 FESEM images of the TiO₂-400 at different magnifications

Figure 6.2 shows the images of TiO₂-400. From the series of images, it is clear that after calcination, the RF was completely burnt off leaving behind monodisperse hierarchical TiO₂ nanorod spheres. This is an obvious advantage over hydrothermal method, which regularly results in the aggregation of nanomaterials. From the enlarged images (Figures 6.2b and 6.2c) of the selected area in Figure 6.2a and the individual TiO₂ nanorod sphere in Figure 6.2d, it provides evidence that the TiO₂ nanorod spheres have uniform dimensions. The diameter of these spheres is approximately 50 nm–1 μ m, while the length and the diameter of TiO₂ nanorods and

their comprising spheres are approximately 250 nm–500 nm, and tens of nanometers, respectively.

Figure 6.3 FESEM images of TiO₂-500 at different magnifications

Similar to Figure 6.2, the FESEM images in Figure 6.3 of the TiO₂-500 had the same structural characteristics as Ti-400. Additionally, both Figures 6.2 and 6.3 revealed that hierarchical TiO₂ nanorod spheres were formed from the outward growth of TiO₂ nanorods.

Figure 6.4 shows the FESEM images of TiO₂-600. Despite the increase in temperature, the monodisperse hierarchical TiO₂ nanorod spheres still appeared uniform in dimensions and the growth of nanorods originated from the center and

grew outwards before forming into an entire sphere. Therefore, these common characteristics observed for the TiO₂-400, TiO₂-500, and TiO₂-600 provide evidence that the increase in calcination temperature did not damage the morphology TiO₂ nanorod spheres.

Figure 6.4 FESEM images of TiO₂-600 at different magnifications

However when the Ti/RF spheres were calcined at temperature greater than 700 °C, obvious morphology changes of TiO₂ nanorod spheres were observed (Figure 6.5). From the FESEM image, the well defined circular structure of TiO₂ nanorod spheres was no longer present. The individual TiO₂ nanorod sphere shown in Figure 6.5b have broken down and the pores between TiO₂ nanorods have been partially blocked. Furthermore from the high magnification FESEM images in Figure 6.5c and 6.5d, it shows that the TiO₂ nanorods did not appear as distinct and sharp. Thus it can be

concluded that calcination at 700 °C would destroy the morphology of TiO₂ nanorod spheres.

Figure 6.5 FESEM images of TiO₂-700 at different magnifications

Figure 6.6 and Figure 6.7 shows the FESEM images of the TiO₂-800 and TiO₂-900, respectively. Observed from the images, the increase in calcination temperature had severely damaged the structure of TiO₂ nanorod spheres. Further investigation using the LBE detector revealed though the TiO₂ nanorod spheres are still visible, most of the pores between TiO₂ nanorods have been blocked,

Figure 6.6 FESEM images of TiO_2 -800 at different magnifications

Figure 6.7 FESEM images of TiO_2 -900 at different magnifications

The prevailing difference between the TiO₂-900 and TiO₂-800 was that the TiO₂ nanorod spheres were no longer visible after the calcination process. The enlarged images (Figure 6.7c & 6.7d) showed that the TiO₂ nanorod spheres began to form aggregates due to the complete breakdown of TiO₂ nanorods.

Therefore, this shows that the calcination temperature has a significant influence on the resultant morphology of TiO₂ nanorod spheres. When the Ti/RF spheres were calcined at temperatures below 600 °C, it promoted the formation of monodisperse and hierarchical TiO₂ nanorod spheres by completely burning off the RF. However, when the Ti/RF spheres were calcined at temperatures greater than 700 °C the morphology of the resultant TiO₂ nanorod spheres began to breakdown and collapse. Along with the increase of temperature, these defects in the morphology increase until it reaches complete destruction at a calcination temperature of 900 °C.

6.2.2. Effect of Calcination Temperature on the Crystallization of TiO₂

Nanorod Spheres

Figure 6.8 XRD Patterns of TiO₂ nanorod spheres calcined at different temperatures under atmospheric condition

The crystal phase of hierarchical TiO₂ nanorod spheres obtained after calcining the crescent Ti/RF spheres at different temperatures was determined by XRD as shown in Figure 6.8. All the diffraction peaks of TiO₂ nanorod spheres are consistent with the standard tetragonal rutile crystal structure of TiO₂ phase (space group P4₂/mmn; JCPDS file no.21-1276) (Feng et al. 2005, Bai et al. 2012b). However, the intensities of peaks were increased along with the increase of calcination temperature. This indicates that the higher the calcination temperature, the better the crystallization of TiO₂ nanorod spheres will be (Hamadianian et al. 2010).

6.2.3. Effect of Calcination Temperature on Light Absorption Capability

The UV-visible spectra of TiO₂ nanorod spheres were investigated using a UV-vis spectrophotometer and the results are shown in Figure 6.9. An obvious trend was observed between the spectra and calcination temperature. As the temperature increased, it resulted in the red-shifting of the UV-visible spectra of TiO₂ nanorod spheres. This red-shift was a result of the formation of well crystallized TiO₂ nanorod spheres at high temperature. This would result in higher light absorption ability of TiO₂ nanorod spheres.

Figure 6.9 (a) UV-Visible spectra of TiO₂ nanorods sphere calcined at different temperatures, and (b) their corresponding Kubelka-Munk functions

Table 6.1 Band gaps of TiO₂ nanorod spheres calcined at different temperatures

Calcination temperature (°C)	Bandgap (eV)	R ²
400 °C	2.848	0.9858
500 °C	2.846	0.9807
600 °C	2.835	0.9877
700 °C	2.822	0.9803
800 °C	2.759	0.9932
900 °C	2.738	0.9898

After converting the diffusive reflectance measurements into the equivalent absorption coefficient using the Kubelka-Munk function (Bai et al. 2011b), the plot of $(\alpha h\nu)^{1/2}$ against $h\nu$ can be obtained (Figure 6.9b). From Figure 6.9b, the vertical segments of the spectra were extended to intersect $h\nu$ axis (x -axis) to obtain the indirect bandgap (E_g) values of TiO₂ nanorod spheres calcined at different temperatures. The corresponding indirect bandgaps of TiO₂ nanorod spheres calcined at different temperatures were listed out in Table 6.1. The results obtained were consistent with the deduction made from the UV-vis spectra. As the calcination temperature increases, it leads to the formation of well crystallized TiO₂ nanorod spheres. The well crystallized spheres cause the red-shift of UV-visible spectra thus narrowing the indirect bandgaps (i.e. reduce the bandgap) of TiO₂ nanorod spheres.

6.2.4. Effect of Calcination Temperature on Porous Structure and Specific

Surface Area

Figure 6.10 (a) N₂ adsorption/desorption isotherm curves of the TiO₂ nanorod spheres calcined at different temperatures, and (b) their corresponding BJH pore size distribution curves determined by N₂ desorption method

The porous structures of TiO₂ nanorod spheres calcined at different temperatures were measured by N₂ adsorption/desorption method. The N₂ adsorption/desorption isotherm curves of TiO₂ nanorod spheres are shown in Figure 6.10. From the

graphical plots, it was evident that TiO₂ nanorod spheres calcined at different temperatures possess typical mesoporous properties. However, the calcination temperature has an inverse relation to the porous properties of TiO₂ nanorod spheres. As the calcination temperature increases, the volume of TiO₂ nanorod spheres decreased due to the collapse of porous structures. This is in consistence with the observations by FESEM. Moreover, the corresponding BJH pore size distribution curves of TiO₂ nanorod spheres calcined at different temperatures (Figure 6.10b) revealed that prominent peaks were observed at 4 nm for the TiO₂-400, TiO₂-500 and TiO₂-600. This is ascribed to the distances between different TiO₂ nanorods comprising of the spheres. However, no obvious peaks were observed for the TiO₂-700, TiO₂-800, and TiO₂-900 due to the collapse in structural morphology at high calcination temperature.

Table 6.2 BET specific surface areas of TiO₂ nanorod spheres calcined at different temperatures

TiO₂ nanorod spheres	BET specific surface area, m²/g
TiO ₂ -400	70.46
TiO ₂ -500	64.19
TiO ₂ -600	46.60
TiO ₂ -700	34.56
TiO ₂ -800	15.98
TiO ₂ -900	4.32

In addition, the BET specific surface areas of TiO₂ nanorod spheres calcined at different temperatures are listed in Table 6.2 indicating a decreasing trend for the TiO₂ nanorod spheres that were calcined at higher temperatures. This can be

attributed to the reduction in porous structures and collapse of pores between the TiO₂ nanorods.

6.2.5. Effect of Calcination Temperature on PL Spectrum of Hierarchical TiO₂ Nanorod Spheres

Figure 6.11 PL spectrum of hierarchical TiO₂ nanorod spheres calcined at different temperatures

The extent of transfer and separation, as well as the trapping of charge carriers, within the hierarchical TiO₂ nanorod spheres is evaluated by the photoluminescence (PL) emission spectrum. As the PL spectrum shown in Figure 6.11, the calcination temperature obviously affects the transfer behavior of the photogenerated electron and hole. As the calcination temperature increases, the peak intensities become weaker, which reflects the fast transfer and separation of the photogenerated electrons and holes. This is due to the well crystallized TiO₂ nanorod spheres resulted from the high calcination temperature. The well crystallized TiO₂ results in the fast transfer of

electrons, which leads to better separation of electrons and holes. This efficient separation process will retard the recombination of electrons and holes to certain extent, which is favorable for the improvement of photocatalytic activity.

6.3. Summary

In summary, we optimized the effects of calcination temperature and calcination atmosphere (atmospheric and N₂ condition) on TiO₂ nanorod spheres by using a variety of characterization techniques. We provided a detailed analysis on the effect of these factors on the morphology and photocatalytic properties of the resultant TiO₂ nanorod spheres.

The formation of the TiO₂ nanorod spheres under atmospheric conditions was greatly influenced by the calcination temperature. If the spheres were calcined at temperatures greater than 700 °C, the morphology of TiO₂ nanorod spheres would be damaged in terms of the breakdown of TiO₂ nanorods and the collapse of porous structures. This would result in the reduction of porous volume and BET specific surface areas of the hierarchical TiO₂ nanorod spheres.

However, the increase in calcination temperature can promote the crystallization of TiO₂, which will improve the transfer and separation of photogenerated electrons and holes.

CHAPTER 7 PHOTOCATALYTIC WATER PURIFICATION AND CLEAN ENERGY GENERATION BY HIERARCHICAL TiO₂ NANOROD SPHERES

7.1. Introduction

Water and energy crisis are the major challenges to the current and future human civilization. TiO₂ semiconductor heterogeneous photocatalysis has been a promising technology in providing clean water and energy and promoting environmental remediation. The TiO₂ photocatalytic oxidation technology is based on the principle of the holes and electrons generation under light irradiation. The advantage of using the holes for pollutant degradation is to enable it to purify the water but the energy generation through water splitting has been ignored. To fully utilize both holes and electrons, it is necessary to investigate the use of the TiO₂ nanorod sphere for H₂ generation from water and water decontamination processes.

In this chapter, the photocatalytic water purification and clean energy (H₂) generation over the hierarchical TiO₂ nanorod spheres synthesized through high temperature calcination method will be reported. A performance comparison between the hierarchical TiO₂ nanorod spheres synthesized through hydrothermal method and calcination method will be provided. Special discussion was given to the approach on concurrently removal of Cu²⁺ and generating H₂ from wastewater using hierarchical TiO₂ nanorod spheres.

7.2. Photocatalytic Water Purification

7.2.1. Photodegradation of AO7

The hierarchical TiO₂ nanorod spheres calcined at different temperatures were investigated for photocatalytic degradation of AO 7. Figure 7.1 shows the photocatalytic degradation curves of AO 7 by hierarchical TiO₂ nanorod spheres calcined at different temperatures. It was observed about 10 % of AO 7 was removed by the hierarchical TiO₂ nanorod spheres before adsorption equilibrium was reached after 1 hour, with exposure to UV irradiation.

However, it is important to note that UV light naturally photodegrades AO 7 even without the use of photocatalyst. From the photolysis experiment, it was found that approximately 45 % of AO 7 was removed by direct UV irradiation. In comparison to adsorption and photolysis, hierarchical TiO₂ nanorod spheres exhibited higher ability in photocatalytic degrading AO 7. As shown in Figure 7.1, the hierarchical TiO₂ nanorod spheres calcined at different temperatures degraded more than 85 % of AO 7 in 30 min. The photocatalytic degradation curves of AO 7 by hierarchical TiO₂ nanorod spheres calcined at different temperatures were modeled using first-order degradation kinetics to determine the kinetic degradation constant (k, min^{-1}), as listed in Table 7.1. The larger the kinetic constant, the higher the degradation ability of the TiO₂ nanorod spheres. The hierarchical TiO₂ nanorod spheres calcined at different temperatures did not exhibit noticeable changes in the degradation of AO 7 under the testing conditions. This implies that the hierarchical TiO₂ nanorod spheres calcined

at different temperatures have similar photocatalytic activity under UV light irradiation.

Figure 7.1 Photocatalytic degradation curves of AO 7 by the hierarchical TiO₂ nanorod spheres calcined at different temperatures under UV irradiation

Table 7.1 Kinetic constant (k) of photodegradation of AO 7 by the hierarchical TiO₂ nanorod spheres calcined at different temperatures under UV irradiation

TiO ₂ nanorod spheres	Kinetic constant, k (min^{-1})	R^2
Photolysis	0.019	0.9897
TiO ₂ -400	0.061	0.9193
TiO ₂ -500	0.07	0.9489
TiO ₂ -600	0.062	0.9577
TiO ₂ -700	0.057	0.9120
TiO ₂ -800	0.070	0.9741
TiO ₂ -900	0.068	0.9307

7.2.2. Photodegradation of RhB

Similar to the photodegradation of AO 7, the hierarchical TiO₂ nanorod spheres calcined at different temperatures were also investigated for the photodegradation of RhB under UV irradiation. From the photolysis experiment, 15 % of RhB was

degraded when adsorption equilibrium was reached. Furthermore, approximately 43 % of RhB was degraded due to the exposure to UV irradiation.

Figure 7.2 Photocatalytic degradation of RhB by the hierarchical TiO₂ nanorod spheres calcined at different temperatures under UV irradiation

Table 7.2 Kinetic constant (k) of photodegradation of RhB by the hierarchical TiO₂ nanorod spheres calcined at different temperatures under UV irradiation

TiO ₂ nanorod spheres	Kinetic constant, k (min^{-1})	R^2
Photolysis	0.015	0.9867
TiO ₂ -400	0.122	0.9521
TiO ₂ -500	0.107	0.9683
TiO ₂ -600	0.104	0.9655
TiO ₂ -700	0.107	0.9723
TiO ₂ -800	0.118	0.9800
TiO ₂ -900	0.119	0.9634

The photocatalytic degradation curves of RhB by hierarchical TiO₂ nanorod spheres calcined at different temperatures were shown in Figure 7.2. In addition, derived from the first-order kinetic degradation model simulation, the kinetic degradation constant (k , min^{-1}) of TiO₂ nanorod spheres were calculated and listed in Table 7.2. From the

experimental results, it showed that the hierarchical TiO₂ nanorod spheres calcined at different temperatures took 39 min to completely degrade the RhB in the solution. Hence this shows that despite the difference in its calcination temperature, the hierarchical TiO₂ nanorod spheres had similar kinetic degradation constant (k).

Therefore, it can be concluded that hierarchical TiO₂ nanorods spheres calcined at different temperatures generally displayed the same photocatalytic activity for the degradation of AO7 and RhB under UV irradiation. This similar trend was due to several factors which will be explained in the later sections.

7.3. Simultaneously Photocatalytic H₂ Generation and Cu²⁺ Recovery

7.3.1. H₂ Evolution Volume

Figure 7.3 Photocatalytic H₂ evolution by the hierarchical TiO₂ nanorod spheres calcined at different temperatures under atmospheric condition

The photocatalytic H₂ generation activities of the hierarchical TiO₂ nanorod spheres calcined at different temperatures were investigated in the methanol/water sacrificial reagent system with the presence of Cu²⁺ under the irradiation of UV light. The corresponding photocatalytic H₂ evolution curves were presented in Figure 7.3. From Figure 7.3, the hierarchical TiO₂ nanorod spheres calcined at different temperatures generated similar volume of H₂ during the photocatalytic reaction.

7.3.2. H₂ Generation Rate

Figure 7.4 Photocatalytic H₂ generation rates of the hierarchical TiO₂ nanorod spheres calcined at different temperatures

In addition to the H₂ evolution curves shown in Figure 7.3, the corresponding H₂ generation rates of the hierarchical TiO₂ nanorod spheres calcined at different temperatures were also shown in Figure 7.4. The hierarchical TiO₂ nanorod spheres

calcined at different temperatures displayed similar H₂ generation rates under the irradiation of UV light. Clearly, the H₂ generation rates increased at a steady rate during the first 20 min, before it being to stabilize at a constant value of 124.695 $\mu\text{mol}/\text{min}$. Therefore, combining the findings from the H₂ evolution curves and the corresponding H₂ generation rates, the hierarchical TiO₂ nanorod spheres calcined at different temperatures exhibited similar photocatalytic H₂ generation activities.

7.3.3. Cu²⁺ Recovery

Figure 7.5 Cu²⁺ recovery rate in the simultaneous photocatalytic H₂ generation and Cu²⁺ recovery system

The simultaneous process for photocatalytic H₂ generation and Cu²⁺ recovery, holds great potential to tackle the challenges from clean energy generation and environmental purification including organic pollutant degradation and heavy metal recovery (Xu et al. 2011). After the photocatalytic H₂ generation reactions, the Cu²⁺ recovery rates from the reaction solution of the hierarchical TiO₂ nanorod spheres

calcined at different temperatures were obtained with the results shown in Figure 7.5. From the graph, more than 90 % of Cu²⁺ was recovered by the hierarchical TiO₂ nanorod spheres calcined at different temperatures. The Cu²⁺ was recovered through the deposition of metal ions on the surface of TiO₂ nanorod spheres. These Cu²⁺ ions served as the active sites (Xu et al. 2011) for H₂ generation under the irradiation of UV light (Bai et al. 2012b).

7.3.4. Mechanism behind Simultaneous Photocatalytic H₂ Generation and Cu²⁺ Recovery

The FESEM image in Figure 7.6a shows that the TiO₂ nanorod spheres still preserved its original morphology in spite of the deposition of Cu after a 12 hours reaction. The proposed electrons transfer pathway for Cu²⁺ recovery and H₂ generation mechanism on the surface of TiO₂ nanorod spheres is also illustrated in Figure 7.6a. As the electrons in the filled VB of TiO₂ nanorod spheres were excited under UV irradiation, they migrate to the vacant CB, leaving behind holes in the VB (Kudo and Miseki 2009, Xu et al. 2011). Subsequently, Cu²⁺ was reduced into metal Cu and being depositing onto the surface of TiO₂ nanorods (Foster et al. 1993). XPS survey spectra of the TiO₂ nanorod spheres with Cu deposits is shown in Figure 7.6b, which visibly indicate the presence of Cu²⁺ on the surfaces of TiO₂ nanorod spheres. Furthermore, Figure 7.6c supports the findings that the oxidation state of Cu deposited on the surface of the TiO₂ nanorod spheres was +2 in the form of CuO (Liu et al. 2011a). The high resolution XPS spectra of Ti 2p in Figure 7.6d suggests that the oxidation state of Ti is +4 and exists in the form of TiO₂ which is consistent with the high resolution XPS spectra of O1s displayed in Figure 7.6e.

7.3.5. Quantum Efficiency

In order to compare the activity of the photocatalysts used in this study, the quantum yield of the hierarchical TiO₂ nanorod spheres for photocatalytic H₂ generation has to be determined. The apparent quantum yield of the hierarchical TiO₂ nanorod spheres is determined using the following equations.

$$\text{Apparent quantum yield, AQY (\%)} = 100 \times \frac{\text{H}_2 \text{ molecules produced}}{\text{photons supplied}}$$

$$\begin{aligned} \text{No. of H}_2 \text{ molecules generated} \\ = \text{Rate of H}_2 \text{ generation} \times \text{Avogadro's constant} \end{aligned}$$

$$\text{Power of lamp source} = 400W$$

$$\text{Energy of one 365 nm photon, } E = \frac{hc}{\lambda} = 5.4424 \times 10^{-19}J$$

Where,

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ m}^2\text{kg/s},$$

$$c = \text{Speed of light} = 2.2998 \times 10^8 \text{ m/s},$$

$$\lambda = \text{Wavelength} = 365 \times 10^{-9} \text{ m}$$

$$\text{Total no. of photons supplied by lamp} = \frac{\text{Power of lamp source}}{\text{Energy of one 365 nm photon}}$$

$$\begin{aligned} \text{Total no. of photons supplied by lamp} &= \frac{400W}{5.4424 \times 10^{-19}J} \\ &= 7.3497 \times 10^{20} \text{ photons/s} \end{aligned}$$

$$\text{Apparent quantum yield, AQY (\%)} = 100 \times \frac{\text{H}_2 \text{ molecules produced}}{\text{photons supplied}}$$

Using the equations shown, the apparent quantum efficiencies of the hierarchical TiO₂ nanorod spheres calcined at different temperatures corresponding to the H₂

generation rates at different reaction moments were calculated as listed in the Table 7.3.

Table 7.3 Apparent Quantum Efficiency (%)

Time (min)	TiO₂- 400	TiO₂- 500	TiO₂- 600	TiO₂- 700	TiO₂- 800	TiO₂- 900
5	0.05583	0.05862	0.06141	0.067	0.06141	0.06141
40	0.17308	0.17028	0.16805	0.16917	0.17140	0.16749
80	0.16973	0.16191	0.16191	0.17308	0.16861	0.17140

7.3.6. Mechanism Explanation

From the experimental results, the hierarchical TiO₂ nanorod spheres calcined at different temperatures exhibits similar activities for photocatalytic water purification in terms of photodegradation of AO 7 and RhB, and photocatalytic H₂ generation in a methanol/water sacrificial reagent system with the presence of Cu²⁺. The similar photocatalytic activities of the hierarchical TiO₂ nanorod spheres calcined at different temperatures are attributed to several factors such as crystallization, UV-visible spectra, indirect bandgaps, porous property, BET specific surface area and hierarchy of the TiO₂ nanorod spheres. These properties have significant influences on the photocatalytic activity of TiO₂ nanorod spheres. The comprehensive analysis of these properties affected by different calcination temperatures and their corresponding effects on the photocatalytic activity of the TiO₂ nanorod spheres were listed in Table 7.4.

Table 7.4 Comprehensive analysis of the photocatalytic activity of the hierarchical TiO₂ nanorod spheres under the irradiation of UV light

	Changing trends along with the increase of calcination temperature from 400 °C to 900 °C	Effect on photocatalytic activity	Synergic effect
Crystallization	Strengthening	Favorable	
Light absorption ability	Enhancing	Favorable	
Inter band gap (eV)	Narrowing	Favorable	
Porous property	<i>Pore volume</i> Reducing	Unfavorable	Similar photocatalytic activity
	<i>Pore size</i> Pore collapsing	Unfavorable	
BET specific surface area	Reducing	Unfavorable	
Hierarchy	Weakening	Unfavorable	

Through this study, it was observed that the increase in calcination temperature will promote the crystallization of hierarchical TiO₂ nanorod spheres, red-shift of the UV-visible spectra and the narrowing of indirect bandgaps, which are all favorable in the improvements of the photocatalytic activity of TiO₂ nanorod spheres. On the contrary, the increase in calcination temperature will alter the porous property of hierarchical TiO₂ nanorod spheres by reducing the pore volume and pore size, BET specific surface areas and the hierarchy of TiO₂ nanorod spheres which are unfavorable changes. Therefore the combination of these competing effects of the favorable and unfavorable factors ultimately results in the similar photocatalytic activities of the hierarchical TiO₂ nanorod spheres calcined at different temperatures.

7.4. Comparison of Hierarchical TiO₂ Nanorod Spheres Synthesized by Hydrothermal Method and Calcination Method

This section of the thesis will draw comparisons between the hierarchical TiO₂ nanorod spheres synthesized by low temperature hydrothermal method (TiO₂-H) and the hierarchical TiO₂ nanorod spheres fabricated by high temperature calcination method at 500 °C (TiO₂-C).

7.4.1. Comparison of its Characteristic Properties

FESEM was firstly employed to study the morphologies of the TiO₂-H and TiO₂-C. The difference between the images shown in Figure 7.7a and 7.7d signifies that the hydrothermal method easily causes aggregation of the resultant TiO₂ nanorod spheres. However, the high temperature calcination method favorably promotes the formation of monodisperse TiO₂ nanorod spheres. In addition from Figure 7.7b and Figure 7.7e, typical hierarchical structures were observed for both TiO₂-H and TiO₂-C. The distances between different TiO₂ nanorod spheres are in the range of micrometer scale, while the distances between different TiO₂ nanorods are in the range of nanometer scale. Such hierarchical TiO₂ nanorod spheres possess great potentials for providing more reaction sites for oxidation reactions to occur, thus promoting fast mass transfer and allowing more light reflection and multiple scattering within its interior (Bai et al. 2010, Pan et al. 2008, Fonzo et al. 2009).

Figure 7.7 FESEM image of (a)-(c) TiO₂-H, and (d)-(e) TiO₂-C at different magnifications, in contrast, (a) and (d) are the overview images, (b) and (e) are the enlarged images, and (c) and (f) are the individual image of TiO₂-H and TiO₂-C, respectively

From the XRD patterns in Figure 7.8, TiO₂-H and TiO₂-C have the standard tetragonal rutile structure (space group P4₂/mm; JCPDS file no. 21-1276) (Bai et al. 2010, Feng et al. 2005, Bai et al. 2012b). This is due to the use of the same titanium precursor (TiCl₃) in the preparation of the hydrothermal precursor and the Ti/RF spheres for high temperature calcination method. Comparing the enhanced XRD peaks of TiO₂-C and TiO₂-H, the high temperature calcination strengthen the crystallization of TiO₂ compared to the low temperature hydrothermal process. The well crystallization of TiO₂ is the advantage of the high temperature calcination method over hydrothermal method, as well crystallized TiO₂ is a favorable improvement for the photocatalytic activity (Hamadianian et al. 2010).

Figure 7.8 XRD patterns of TiO₂-H and TiO₂-C

The UV-visible spectrum of TiO₂-H and TiO₂-C were investigated using a UV-vis spectrophotometer and shown in Figure 7.9. In comparison to TiO₂-H, TiO₂-C exhibited stronger light absorption capability in both UV and visible range. This is as a result of the well crystallized TiO₂ nanorod spheres obtained from the high temperature calcination method (Hamadanian et al. 2010). The diffusive reflectance measurements were converted into the equivalent absorption coefficient using the Kubelka-Munk function (Liu et al. 2011a, Bai et al. 2011b, Ng et al. 2010).

Figure 7.9 UV-visible spectra of TiO₂-H and TiO₂-C, the inset is the corresponding Kubelka-Munk transformed reflectance

The inset in Figure 7.9 shows the $(\alpha h\nu)^{1/2}$ plotted versus $h\nu$ and the vertical segment of the spectra is extended to intersect $h\nu$ axis (x -axis) to obtained the indirect bandgap (E_g) values of TiO₂-H and TiO₂-C. Evidently, TiO₂-C had a slightly narrower indirect bandgap in a comparison to that of TiO₂-H, although they possess the same hierarchical structures. This reflects the advantage of high temperature calcination method in allowing TiO₂ to be easily excited under irradiation over hydrothermal method. This enhanced light absorption capability and narrowed indirect bandgap are both favorable improvements made to enhance the photocatalytic activity of TiO₂-C.

Figure 7.10 PL spectrum of TiO₂-H and TiO₂-C excited at 320 nm

Figure 7.10 depicts the PL spectrum of TiO₂-H and TiO₂-C with an excitation at 320 nm to compare the extent of transfer and separation of the photogenerated electrons and holes on the surface of hierarchical TiO₂ nanorod spheres. It can be seen that TiO₂-C has a lower PL intensity in a comparison to TiO₂-H. The lower intensity of TiO₂-C reflects its stronger ability in promoting electrons transfer and thus suppressing the recombination of photogenerated electrons and holes. The rationale behind this lies in the formation of well crystallized TiO₂ obtained from the high temperature calcination method. Thereby, the efficient anti-recombination of photogenerated electrons and holes of TiO₂-C is also a favorable factor for improving the photocatalytic activity of TiO₂-C (Liu et al. 2007a, Ng et al. 2010).

Figure 7.11 N₂ adsorption/desorption isotherm curves of TiO₂-H and TiO₂-C, and (b) their corresponding pore size distribution curves determined by BJH N₂ desorption method

The porous structures of TiO₂-H and TiO₂-C were measured by N₂ adsorption/desorption isotherm method as shown in Figure 7.11a. Both TiO₂-H and TiO₂-C have typical mesoporous properties (Chen et al. 2011b, Bai et al. 2012c). Figure 7.11b presents the BJH pore size distribution curves of TiO₂-H and TiO₂-C. A dominant peak was observed at 4 nm and a minor peak was seen at 7 nm for TiO₂-

C. This can be ascribed to the distances between different TiO₂ nanorods comprising of spheres.

For TiO₂-H, the dominant peak was also observed at 4 nm, however the minor peak was observed at 11 nm. The slight difference of pore size distributions between TiO₂-H and TiO₂-C reflects that calcination method easily produces TiO₂ nanorod spheres with uniform pore size distribution in comparison to hydrothermal method. The BET specific surface areas of TiO₂-C and TiO₂-H were measured to be 64.19 m²/g and 44.73 m²/g, respectively. The larger specific surface area of TiO₂-C over TiO₂-H is another favorable factor in improving the photocatalytic activity through the provision of more reaction sites which enhances the mass transfer inside the hierarchical TiO₂ nanorod spheres (Bai et al. 2010).

7.4.2. Photocatalytic Water Purification

The photocatalytic activities of TiO₂-C and TiO₂-H were compared through investigating their capabilities in degrading pollutants under the irradiation of UV light. Here AO 7 and RhB were used as the probe pollutants. For the case of AO 7 degradation, about 10 % AO 7 was removed by the adsorption of TiO₂-H and TiO₂-C for 1 hour without UV irradiation, which indicates that two kinds of TiO₂ have the similar adsorption capabilities due to their similar mesoporous properties and BET specific surface areas. However the removal of AO 7 was obviously enhanced with the presences of TiO₂-C and TiO₂-H under UV irradiation. The photocatalytic degradation curves of AO 7 by TiO₂-C and TiO₂-H presented in Figure 7.12 shows

that TiO₂-C can completely photodegrade AO 7 in 40 min, while only about 83 % of AO 7 was photodegraded by TiO₂-H under the same conditions. The first-order kinetic degradation equations were used to simulate the photodegradation curves of AO 7 by TiO₂-C and TiO₂-H so as to obtain the kinetic rate constant (k , min^{-1}) as listed in Table 7.6. The kinetic rate constant k for AO 7 degradation by TiO₂-C is larger than that by TiO₂-H, which indicates that TiO₂-C exhibits better photocatalytic activity than TiO₂-H.

Figure 7.12 Kinetic degradation curves of AO7 by TiO₂-H and TiO₂-C under the same testing conditions

For the photodegradation of RhB, 15 % of RhB was removed as a result of adsorption by TiO₂-C and TiO₂-H after 1 hour without UV irradiation. And the direct UV irradiation for 50 min resulted in 43 % degradation of RhB. But the degradation rates of RhB were greatly enhanced by the additions of TiO₂-C and TiO₂-H under UV irradiation. The photocatalytic degradation curves of RhB by TiO₂-C and TiO₂-H were plotted and shown in Figure 7.13. It can be seen that TiO₂-C can completely

degrade the RhB after UV irradiation for 50 min, while only about 90 % of RhB was degraded by TiO₂-H. Through the modeled first-order degradation kinetics, the kinetic rate constants (k , min^{-1}) for the photodegradation of RhB by TiO₂-C and TiO₂-H were of 0.08 min^{-1} and 0.045 min^{-1} respectively. This higher kinetic rate constant clearly reflects the better photocatalytic activity of TiO₂-C than TiO₂-H.

Figure 7.13 Kinetic degradation curves of RhB by TiO₂-C and TiO₂-H under the same conditions

Table 7.5 Kinetic rate constants (k) for the photodegradation of AO 7 and RhB by TiO₂-C and TiO₂-H

	AO 7	RhB
TiO₂-H	0.043	0.045
TiO₂-C	0.094	0.080

7.4.3. Photocatalytic H₂ Generation

Figure 7.14 Photocatalytic H₂ generation curves of TiO₂-H and TiO₂-C

The photocatalytic H₂ generation curves of the TiO₂-C and TiO₂-H presented in Figure 7.14 reveals that TiO₂-C exhibited better photocatalytic activity for H₂ generation than TiO₂-H in the methanol/water methanol sacrificial reagent system with the presence of Cu²⁺ under the irradiation of UV light. Although the H₂ generation volume of TiO₂-C and TiO₂-H accumulated at constant rates, the rate at which H₂ was accumulated by TiO₂-C is faster than that of TiO₂-H due to its improved photocatalytic activity.

The higher photocatalytic activity of TiO₂-C than TiO₂-H is due to the following merits. First, TiO₂-C is better crystallized than TiO₂-H. This well defined crystalline structure improved the light absorption capability, narrowed the indirect bandgap and

promoted the electrons transfer of TiO₂-C. Second, the monodisperse TiO₂-C possesses more reaction sites for oxidation reactions to take place compared to the aggregated TiO₂-H. Third TiO₂-C had a relatively larger light absorption capability and specific surface areas than TiO₂-H. Lastly, the well crystallized TiO₂-C allowed efficient transfer of electrons thus suppressing the recombination of photogenerated electrons and holes and therefore leading to higher photocatalytic activity.

7.5. Summary

In summary, this chapter investigated the photocatalytic water purification and photocatalytic H₂ generation capabilities of the hierarchical TiO₂ nanorod spheres calcined at different temperatures. From the experimental results, the hierarchical TiO₂ nanorod spheres exhibited higher photocatalytic activity for water purification in terms of degrading pollutants. These hierarchical TiO₂ nanorod spheres also demonstrated high photocatalytic activities for the simultaneous photocatalytic H₂ generation and Cu²⁺ recovery from wastewaters under the irradiation of UV light. The results demonstrated that the hierarchical TiO₂ nanorod spheres calcined at different temperatures had similar photodegradation abilities of AO 7 and RhB under the irradiation of UV light, and similar photocatalytic H₂ generation activities and Cu²⁺ recovery abilities in a simultaneous system. This similar photocatalytic activities of hierarchical TiO₂ nanorod spheres calcined at different temperatures was due to the competing effects of several factors. Thus it can be suggested that the calcination temperature at 500 °C is the optimal calcination temperature for a cost effective fabrication of hierarchical TiO₂ nanorod spheres using the high temperature calcination method.

Also reviewed in this chapter were the effects of the fabrication method on the photocatalytic activity of the hierarchical TiO₂ nanorod spheres. Through the characteristics comparisons, the high temperature calcination method easily produced monodisperse and well crystallized hierarchical TiO₂ nanorod spheres compared to the hydrothermal method. The hierarchical TiO₂ nanorod spheres fabricated by high temperature calcination method also resulted in the red-shift of UV-vis spectra, and enlarged the BET specific surface areas. Therefore, the hierarchical TiO₂ nanorod spheres fabricated by high temperature calcination method exhibited better photocatalytic activity for water purification and H₂ generation. Considering these factors, it proves that the high temperature calcination method is able to fabricate hierarchical TiO₂ nanorod spheres with consistent morphology on large scale. Therefore it is evident that the high temperature calcination method possesses many advantages over the hydrothermal method both in materials synthesis and photocatalytic water purification and simultaneous clean energy generation and Cu²⁺ recovery.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1. Conclusions

8.1.1. Hydrothermally Synthesized Hierarchical TiO₂ Nanorod Spheres

To the best of our knowledge, the fabrication of TiO₂ nanorod spheres without the assistance of template has not been reported to date. We have successfully synthesized the hierarchical TiO₂ nanorod spheres via a facile template-free low temperature hydrothermal method. Besides the presence of anatase TiO₂, rutile TiO₂ can also be identified by creating a strong acidic condition through adjusting the pH of the precursor. The Cl⁻ from the supersaturated precursor solution containing NaCl plays a significant role in controlling the growth of TiO₂ along [001] direction. The dimension of the synthesized TiO₂ nanorod spheres is around 500 nm~1 μm, while the length and diameter of the TiO₂ nanorods with attachment of the spheres are approximately tens of nanometers and hundreds of nanometers, respectively. Meanwhile, the synthesized TiO₂ nanorod spheres have typical hierarchical structure, in which: the distances between different TiO₂ nanorod spheres are in the range of micrometer scale, while the distances between different TiO₂ nanorods comprising of the spheres are in the range of nanometer scale. The hierarchical TiO₂ nanorod spheres contain typical mesoporous properties with larger BET specific surface areas. As a result, the TiO₂ nanorod spheres are capable of promoting faster mass transfer and providing larger reaction sites for oxidation reactions taking place compared to TiO₂ P25. Meanwhile, the hierarchical TiO₂ nanorod spheres also slightly red-shifted

the UV-vis spectra in a comparison to TiO₂ P25 owing to its hierarchical structure allowing more light reflection and multiple scattering inside the interior.

By integrating the hierarchical TiO₂ nanorod spheres with a membrane filtration, an innovative “*win-win*” strategy was developed for water purification. A novel multifunctional membrane is created via assembling hierarchical TiO₂ nanorod spheres uniformly onto a piece of polymer membrane, the functional layer is structured by hierarchical TiO₂ nanorod spheres. This hierarchical TiO₂ nanorod membrane exhibits strong capability for photocatalytic water purification by maximizing the photodegradation ability of TiO₂ nanorod spheres and improving the rejection ability of membrane. For example, membrane can recover TiO₂ while TiO₂ can mitigate the membrane fouling under the irradiation of UV light.

Under the same testing conditions, the TiO₂ nanorod spheres structured membrane exhibited identical photodegradation ability of HA and MB as TiO₂ P25 deposited membrane under the irradiation of UV light. In addition, the TiO₂ nanorod membrane also exhibits higher permeates flux as compared to TiO₂ P25 deposited membrane. This can be explained by the porous functional layer created by hierarchical TiO₂ nanorod spheres. In comparison with the dense layer formed by TiO₂ P25, this porous functional layer allows water to pass through easily. As a consequence, the TiO₂ nanorod membrane is capable of purifying wastewater at a minimal fouling state. The experimental results demonstrated the effectiveness of hierarchical TiO₂ nanorod membrane that will perform water purification at a minimal membrane fouling, high

flux and high water quality manner. Both the innovations in the synthesis of hierarchical TiO₂ nanorod spheres and the application for concurrent photocatalytic membrane filtration contributed greatly to the scientific research and industrial application.

8.1.2. High Temperature Calcination Fabricated Hierarchical TiO₂ Nanorod Spheres

In order to overcome the drawbacks of hydrothermal method for the synthesis of hierarchical TiO₂ nanorod spheres, facile high temperature calcination method is introduced to fabricate hierarchical TiO₂ nanorod spheres. This method is demonstrated by deliberately adding TiCl₃ into the resorcinol and formaldehyde reaction. In comparison to the low temperature hydrothermal method, the high temperature calcination method is able to fabricate monodisperse, well crystallized hierarchical TiO₂ nanorod spheres on large scale. This method covers two steps: (1) the formation of crescent Ti/RF spheres in an open reactor under heating and stirring, and (2) the calcination of crescent Ti/RF spheres leading to the formation of hierarchical TiO₂ nanorod spheres. With careful control of the concentration of resorcinol, formaldehyde and TiCl₃ in the precursor, the resultant rutile TiO₂ grew along the [001] direction with influence of Cl⁻. Next, the RF spheres act as template which *in-situ* wrapped up the TiO₂ nanorods into crescent Ti/RF spheres. Under the atmospheric condition, the latter calcination of crescent Ti/RF spheres promotes the formation of well crystallized hierarchical TiO₂ nanorod spheres via burning off the RF spheres. The calcination of crescent Ti/RF spheres under the N₂ condition resulted

in the coexistence of hierarchical TiO₂ nanorod spheres and carbon spheres owing to the carbonization of RF spheres.

The calcination temperature plays a significant role in determining the hierarchical TiO₂ nanorod spheres and its photocatalytic performance. The increase of calcination temperature promotes the crystallization of TiO₂ nanorod spheres, the red-shift of UV-vis spectra narrows the indirect bandgaps to favor the photocatalytic activity. The calcination with temperature less than 600 °C will result in well defined hierarchical TiO₂ nanorod spheres without damaging its morphology. However, calcination with temperature higher than 700 °C damage the hierarchical structure of TiO₂ nanorod spheres via breaking down the TiO₂ nanorods. As a result, the porous volume and BET specific surface areas are reduced which affect the photocatalytic activity. The hierarchical TiO₂ nanorod spheres were investigated for photocatalytic water purification in terms of degrading AO 7 and RhB, and photocatalytic H₂ generation in a methanol/water sacrificial reagent system under the irradiation of UV light. The experimental results show that the hierarchical TiO₂ nanorod spheres calcined under different temperatures exhibited similar photocatalytic activities. The similar photocatalytic activities are ascribed to the comprehensively competing effects of all those favorable and unfavorable factors affected along with the increase of calcination temperature. Therefore, in view of the fabrication cost, it is suggested that the calcination at 500 °C is the optimal option for the synthesis of hierarchical TiO₂ nanorod spheres.

The characteristic properties and the photocatalytic performance of the hierarchical TiO₂ nanorod spheres synthesized by low temperature hydrothermal method and high temperature calcination method are also investigated. It is found that the high temperature calcination method would result in monodisperse and well crystallized TiO₂ nanorod spheres as compared to the hydrothermal method. Meanwhile, the hierarchical TiO₂ nanorod spheres fabricated by high temperature calcination method would red-shift the UV-vis spectra and reduce the PL intensity in a comparison to that synthesized by hydrothermal method, and thus exhibit higher photocatalytic activity. Hence, high temperature calcination is a promising approach for the fabrication of hierarchical TiO₂ nanorod spheres for photocatalytic water purification and H₂ generation. Therefore, this method is considered to be suitable for practical industrial application.

8.1.3. The Merits of Hierarchical TiO₂ Nanorod Spheres Over Benchmark

TiO₂ P25

In this study, we successfully developed two methods (low temperature hydrothermal method and facile calcination method) to synthesize hierarchical TiO₂ nanorod spheres and used them for clean water and energy generation. The synthetic mechanisms were explained in details by using a variety of characterization techniques. Their performances in clean water and energy generation were evaluated. It reveals that the hierarchical TiO₂ nanorod spheres exhibit better performances than commercial TiO₂ P25. It is reasonable to believe that the developed methods are of great significances to promote the synthesis of hierarchical structured TiO₂ and widen their applications in clean water and energy field. Table 8.1 summarizes the detailed

comparisons between the hierarchical TiO₂ nanorod spheres with commercial TiO₂ P25 from the aspects of synthesis method, characteristics, properties and performances. This table is to highlight the advantage of our developed hierarchical TiO₂ nanorod spheres over TiO₂ P25. Hierarchical TiO₂ nanorod spheres developed by our two methods (low temperature hydrothermal method and calcination method) not only can be produced on industrial scale, but also can exhibit many advantages over TiO₂ P25. This guarantees their promising futures in materials synthesis and practical engineering applications.

Table 8.1 The merits of hierarchical TiO₂ nanorod spheres over benchmark TiO₂ P25

		TiO₂ P25	TiO₂-H	TiO₂-C
Synthesis	Origin	Degussa	Developed in this study	Developed in this study
	Method	H ₂ gas Flame combustion method	Low temperature Hydrothermal method	Calcination method
	Mechanism	$\text{TiCl}_4 + \text{H}_2 + \text{O}_2 \leftrightarrow \text{TiO}_2 + 4\text{HCl}$	1) $\text{TiCl}_3 \rightarrow \text{Ti}^{3+} + 3\text{Cl}^-$; $\text{Ti}^{3+} + \text{O}_2 \rightarrow \text{TiO}_2$ 2) TiO ₂ slowly formed and grew along the preferred orientation, and 3) the growing TiO ₂ nanorods self-assembled into spheres	1) $\text{TiCl}_3 \rightarrow \text{Ti}^{3+} + 3\text{Cl}^-$; $\text{Ti}^{3+} + \text{O}_2 \rightarrow \text{TiO}_2$ 2) Resorcinol + formaldehyde-RF spheres; $\text{TiO}_2 + \text{RF} \leftrightarrow \text{Ti/RF Spheres}$ 3) $\text{Ti/RF spheres} \leftrightarrow \text{TiO}_2 \text{ nanorod spheres}$
Characteristics	Morphology
	Size	25 nm	500 nm~1 μm	500 nm~1 μm
	Crystal	Anatase/rutile	Rutile	Rutile
	Dispersibility	Aggregation	better ^a	best ^b
	Structure	Nanoparticles	Hierarchical TiO ₂ nanorod spheres	Hierarchical TiO ₂ nanorod spheres
	Carbon coating	no	no	yes

Properties	BET	34.35 m ² /g	44.73 m ² /g	64.19 m ² /g
	Porous property	Mesoporous	Mesoporous	Mesoporous
	Light absorption	UV only	Better ^a	Best ^b
	Lifespan of electrons and holes	Short	Better ^a	Best ^b
Performance	Photodegradation ability	Good	Better ^a	Best ^b
	Flux performance	Low	Better ^c	Better ^c
	Photocatalytic H ₂ generation activity	Low	Better ^a	Best ^b
	Mass production	Yes	Yes ^d	Yes
	Reproducibility	Good	Not good	Excellent

Note: ^a compared with benchmark commercial available TiO₂ P25;

^b compared with TiO₂-H and TiO₂ P25 under the same testing conditions;

^c compared with TiO₂ P25 under the same testing conditions.

^d more works are still needed for mass production, though theoretically feasible.

8.2. Recommendations

8.2.1. Materials Innovation

In this study, we have developed a low temperature hydrothermal method and a facile high temperature calcination method to fabricate hierarchical TiO₂ nanorod spheres. However, further efforts and systematical works are necessary to clearly understand the mechanism and the effect of synthetic conditions on the formation of hierarchical TiO₂ nanorod spheres.

For the low temperature hydrothermal method, systematical works shall be conducted to investigate the influence of pH, concentration of precursors, the hydrothermal temperature and reaction time on the formation of hierarchical TiO₂ nanorod spheres.

For the fabrication of hierarchical TiO_2 nanorod spheres using high temperature calcination method, deep and systematic works are necessary to investigate the influencing factors in formation process and the calcination process of the Ti/RF spheres, which include the concentrations of precursors of resorcinol, formaldehyde and TiCl_3 , and the reaction conditions on the formation of crescent Ti/RF spheres.

For both the hydrothermal method and high temperature calcination method, it is still of great significance to further improve the photocatalytic activity of the hierarchical TiO_2 nanorod spheres through increasing the light absorption capability, efficiently retarding the recombination of photogenerated electrons and holes via doping metal or nonmetal elements.

8.2.2. Clean water and Clean Energy Generation

Hierarchical TiO_2 nanorod spheres demonstrated to be promising for photocatalytic water purification and clean energy generation. However, the journey from the academic research to practical application has to be further explored. In order to accelerate this process, the followings works are recommended:

- Further explorations are necessary to design novel reactors suitable for the photocatalytic water purification and clean energy generation. Ultimately, the reactor will acquire a higher efficiency if it can be excited by solar light.

- Detailed investigation on the application of hierarchical TiO_2 nanorod spheres for photocatalytic water purification as well as revealing the membrane fouling mitigation mechanism will be essential. This will aid in providing improvements for practical engineering application.
- Beside, hierarchical TiO_2 nanorod spheres can also be applied in some other fields such as DSSC, conversion of CO_2 into CH_4 and lithium ion batteries (LIBs), etc. This will further broaden the application of hierarchical TiO_2 nanorod spheres to tackle the global crises.

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