TiO₂ composite nanofiber materials for simultaneous renewable energy production and waste water treatment

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**TiO₂ COMPOSITE NANOFIBER MATERIALS FOR
SIMULTANEOUS RENEWABLE ENERGY
PRODUCTION AND WASTE WATER TREATMENT**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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**TiO₂ Composite Nanofiber Materials for
Simultaneous Renewable Energy Production and
Waste Water Treatment**

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SUMMARY

This study sought to enhance the viability of TiO_2 photocatalysis for concurrent clean energy fuel (hydrogen, H_2) and clean water production; through simplification and/or innovation of synthesis method for TiO_2 composite nanomaterials by exploiting electrospinning.

Advancing from the past research within our group, a green approach was first attempted by integrating the synergy of one-dimensional (1D) ultralong and ultrathin electrospun TiO_2 nanofibers and the photocatalytic treatment of Cu-EDTA wastewater (Approach A). Upon UV-visible light irradiation, Cu-EDTA was oxidized by TiO_2 thus releasing Cu^{2+} which was reduced and recovered through uniform adsorption onto the long and porous TiO_2 surface. The recovered Cu provided active sites for H_2 generation via photo-reduction of H_2O and enhanced photo-oxidation of remaining intermediate oxidation by-products. Interestingly, the used TiO_2 nanofibers deposited with Cu could be reclaimed directly as TiO_2/CuO composite after a facile heat treatment, and even without additional chemical in particular acid which had been used to dissolve and recover the Cu like that reported in the literature before. Experimental result showed that on top of the cogeneration of clean energy and clean water without the addition of methanol (a conventionally used sacrificial reagent for photocatalytic H_2 generation), this approach has also enabled the reclamation of potentially efficient TiO_2/CuO composite from photocatalytic treatment of Cu-EDTA waste water which is available from the industry. This has immediately initiated a green synthesis method for TiO_2/CuO composite. In addition, through an in-depth characterization of the reclaimed $\text{TiO}_2\text{-CuO}$ composite using SEM, TEM, XRD, N_2 adsorption-desorption method, BJH method, BET method, XPS, UV-vis absorbance spectra, and PL spectra, a comprehensive mechanism for this synergistic system was unravelled to bridge the research gap.

Subsequently, electrospinning of an innovative precursor solution (Approach B) was developed to enhance the physicochemical properties while maintaining

procedural simplicity and minimizing resources in the synthesis of TiO₂ composite. Novel-structured TiO₂/CuO composite nanofibers were successfully fabricated through this quest. The composite nanofibers were well characterized by SEM, TEM, XRD, N₂ adsorption-desorption method, BJH method, BET method, XPS, UV-vis absorbance spectra, and PL spectra. Experimental results showed that the nanofibers exhibited greatly enhanced H₂ evolution rate compared to bare TiO₂ nanofiber and P25. Overall, the enhanced efficiency of the composite nanofibers was attributed to their excellent synergistic properties such as: 1) good mesoporosity; 2) the red-shift of absorbance spectra to enhance light absorbance capability; 3) long nanofibrous structure and 4) TiO₂/CuO heterojunctions favorable for the separation of electrons and holes.

TiO₂/CuO composite nanofibers from both Approach A and B were used for simultaneous H₂ and clean water production from other synthetic wastewater under both UV-visible and visible light, to predict their future application and to study their stability and reusability. Both TiO₂/CuO composites exhibited promising photocatalytic efficiency when used to treat industrial wastewater such as glycerol and AO7 for the first time; with sustained stability even after repeated use. Both TiO₂/CuO composite nanofibers exhibited comparable H₂ and clean water generation. Approach B has produced relatively more superior TiO₂/CuO composite compared to Approach A due to better physicochemical properties and stability.

Moving forward, synthesis calcinations temperature for Approach B was varied in order to verify and gain an in-sight of how the balance and synergy among the essential physicochemical properties would influence the photocatalytic efficiency. Calcinations at temperature above and below 450 °C showed negative effect on the H₂ generation. This was ascribed to the effect of temperature on transformation of crystalline phase, crystal growth, mesoporosity formation, and Cu valence state which has thus adversely affected the synergy among the physicochemical properties of TiO₂/CuO composite nanofibers. Meanwhile, leachability of Ti and Cu was found to reduce with higher calcinations temperature. Further optimization of electrospun TiO₂/CuO composite nanofibers (from Approach B) showed that

TiO₂/CuO composite nanofibers with 6 % mol Cu, calcined at 450 °C for 45 min, exhibited the highest H₂ generation.

Significant scientific contributions from this research study are as follows:

A green approach was demonstrated for the first time to cogenerate H₂ and clean water concurrently via the synergy of integrating one-dimensional (1D) ultralong and ultrathin electrospun TiO₂ nanofibers and the photocatalytic treatment of Cu-EDTA wastewater. The mechanism behind this approach was presented for the first time. This approach exhibited significant environmental benefits as it enables not only cogeneration of clean energy fuel and clean water but also the reclamation of TiO₂/CuO composite potentially usable for other environmental application, thus offering a simplified yet green route to produce TiO₂/CuO composite.

New precursor solution blends were successfully introduced for the electrospinning of TiO₂ composite nanofibers. The synthesis procedure did not require high temperature, high speed mixing or dispersive equipment, and corrosive chemicals as reported before by others for TiO₂ composite nanofibers synthesis; thus making it an even more attractive, economical and environmental friendly method.

For the first time, successful structure innovation with incorporation of essential physical and chemical properties as follows in TiO₂/CuO composite nanofibers (from Approach B) was demonstrated through electrospinning of the new precursor solution:

- Consistent and long nanofibrous structure composed of granular nanocrystals, with high aspect ratio. This promotes interparticle charge transfer along the long nanofibrous structure,
- Smaller anatase TiO₂ crystal size promoted by Cu loading is advantageous because it renders higher contact area with TiO₂ and shorter migration distance for photogenerated charge transfer to the surface reaction sites and thus lowers the recombination rate.

- Highly dispersed Cu in respective composite nanofibers which ensure good contact between TiO_2 and CuO serves to enhance the photogenerated electrons and holes transfers between the heterojunctions.
- Increased porosity and specific surface area promotes light absorption and utilization; and reactants adsorption; thus facilitating mass transfer and interfacial charge transfer for an efficient heterogeneous photocatalysis.
- Red-shift of the composite nanofibers extends the photocatalysts' ability to utilize the light energy source from UV range into visible range.
- Minimized recombination rate of photogenerated electrons and holes owing to the heterojunctions formed in the composite nanofibers, thus promoting the charge migration and separation.

For the first time, the H_2 generation capabilities of TiO_2/CuO composite nanofibers (both Approach A and B) were demonstrated to be more superior to their pristine and composite nanoparticle counterpart in glycerol and AO7.

In summary, this study is significant as it has demonstrated and expounded innovative approaches which enhanced the environmental sustainability of cogenerating clean energy fuel and clean water from industrial wastewater through TiO_2 photocatalysis.

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Journal

1. **S. S. Lee**, H. W. Bai, Z. Y. Liu, and D. D. Sun (2012) "Electrospun TiO₂/SnO₂ Nanofibers with Innovative Structure and Chemical Properties for Highly Efficient Photocatalytic H₂ Generation", *International Journal of Hydrogen Energy*, 37(14), 10575-10584 (**IF:2.930**)
2. **S. S. Lee**, H. W. Bai, Z. Y. Liu, and D. D. Sun (2012) "Novel-Structured Electrospun TiO₂/CuO Composite Nanofibers for High Efficient Photocatalytic Cogeneration of Clean Water and Energy from Dye Wastewater", *Water Research*, 47(12), 4059-4073 (**IF:5.323**)
3. **S. S. Lee**, H. W. Bai, Z. Y. Liu, and D. D. Sun (2013) 'Optimization and an Insightful Properties-Activity Study of Electrospun TiO₂/CuO Composite Nanofibers for Efficient Photocatalytic H₂ Generation', *Applied Catalysis B: Environmental*, Vol 140-141, Aug-Sept 2013, 68-81 (**IF:6.007**)
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2. **S. S. Lee**, H. W. Bai, Z. Y. Liu, and D. D. Sun (2013) "One-dimensional electrospun TiO₂-based composite nanofibers-paving an avenue to resource recovery from wastewater" Oral Presentation, IWA Symposium on Environmental Nanotechnology, April 24-27, 2013, Nanjing, China.
3. **S. S. Lee** and D. D. Sun (2013). "Novel electrospun TiO₂/CuO composite nanofibers - towards a sustainable resource recovery from wastewater", Oral Presentation, 8th Asia-Oceania Top University League on Engineering

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CHAPTER 1 INTRODUCTION

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1.1 Background

Energy and environment are two global major challenges today. Population and economic growth as well as technological development are the main energy source drivers, with fossil fuel being the most popular and economical. However, fossil fuel is a non-renewable resource, and thus it is bound to depletion in a matter of

time. The world reserves are predicted to last us another 30-40 years for oil and natural gas and 400-450 years for coal (Getoff 1990, Liu, Burghaus et al. 2010). On top of that, the consumption of fossil fuels presents the threat of climate change due to the air emission of green house gases such as CO₂, NO₂ and CH₄ (Schloegl 2008, Chen, Shen et al. 2010). It is well-known that climate change is also associated with the risk of reducing freshwater supply and its quality owing to alterations of precipitation patterns and evaporation rates from the rising atmospheric temperature (Lee, Bai et al. 2012). Consequently, water scarcity problem which is already afflicted by the burgeoning population and industrialization will be further aggravated by climate change.

In response to the pressing global warming issue from the utilization of fossil fuel, hydrogen (H₂) as an ideal clean energy source has attracted large attention by researchers (Zou, Ye et al. 2001). H₂ is a very attractive fuel source due to its zero carbon emission, high conversion efficiencies, and it can be easily produced and stored on site (Lee, Bai et al. 2013). It offers immense potential as a clean and renewable energy source which may alleviates the reliance on fossil fuels. Photocatalytic H₂ generation from water splitting is one of the promising long-term solutions to generate H₂ (Getoff 1990, Kudo and Miseki 2009, Chen, Shen et al. 2010) due to a few attributes: (1) it exploits the renewable solar energy with no threats of resource exhaustion, and (2) it is emission-free thus there is low pollution risk and zero greenhouse gas effect (Kudo and Miseki 2009, Chen, Shen et al. 2010). TiO₂-based semiconductor has been widely-studied for H₂ production since it was first reported by Fujishima and Honda in 1972 (Fujishima and Honda 1972, Kruczynski, Gesser et al. 1981, Ashokkumar 1998, Nada, Barakat et al. 2005, Banerjee 2011). This process is relatively low-cost, does not generate harmful secondary by-product, operable under standard atmospheric condition and utilizes the renewable solar energy for its activation (Chong, Jin et al. 2010). Furthermore, TiO₂ is non-toxic and exhibits high chemical and thermal stability (Hernández-Alonso, Fresno et al. 2009). However, it has inherent rapid recombination of photo-generated electron-hole pairs and wide band gap (Chen and Mao 2007) resulting in low photocatalytic activity for the production of H₂ from water which restricts its

practical applications. Moreover, evolved H_2 and O_2 from water splitting can recombine easily to form H_2O thus lowering the efficiency of H_2 production from photocatalytic water splitting. Meanwhile, the efficiency of TiO_2 could be affected adversely by intermediate by-products and heteroatom contaminant containing N,S,P, or Si atom. This phenomena, usually termed as photocatalysts poisoning, has been reported to adversely affect activity of TiO_2 thus reducing its reusability potential if the poisoning is irreversible (Peral and Ollis 1997, Dutta, Parsons et al. 2009).

Different strategies have been explored to improve photocatalytic H_2 generation from water using TiO_2 . Addition of chemical or sacrificial reagent such as methanol, ethanol, glycerol, and $\text{S}^{2-}/\text{SO}_3^{2-}$ into the reaction solution have been reported to enhance photocatalytic reaction (Daskalaki, Antoniadou et al. 2010, Lianos 2011). Sacrificial reagent reacts as electron donor which will scavenge photogenerated hole in the reaction system thus enriching the photogenerated electrons in a photocatalyst for a more efficient H_2 generation. Among all, the most commonly used sacrificial reagent is methanol (Wu and Lee 2004, Xu, Ng et al. 2010, Lianos 2011). However, since methanol and even some other reagents are also a valuable fuel resources, research should focus on finding new alternatives to reduce if not eliminate the dependence on useful chemical. One attractive approach which has drawn research attention is the use of organic pollutant which is readily available in the industrial organic wastewaters such as EDTA (Kim and Choi 2010), phenol (Kim and Choi 2010), glycerol (Yu and Ran 2011) and azo-dye (Patsoura, Kondarides et al. 2006). In this case, organic pollutant will be degraded by photogenerated hole instead, if the valence band of TiO_2 photocatalyst is more electropositive than the oxidation potential for the organic pollutant of concern (Litter 1999). Meanwhile, H_2O could be reduced to form H_2 if the conduction band of TiO_2 is more electronegative than H_2O reduction potential. Hence, not only H_2 could be generated to possibly minimize the energy demand and cost, a cleaner water could also be obtained concomitantly as a result of the pollutant degradation thus providing an avenue for water reuse which minimizes freshwater demand from the industry of concerned. This in turn could help ameliorate both the looming

energy crisis and water scarcity problem in years to come. Nevertheless, the study on integrating pollutant decomposition and H₂ production over TiO₂ is still lacking despite the encouraging results from the open literature.

Meanwhile, modification of TiO₂ photocatalyst physically and/or chemically are also among the conventionally adopted approaches to improve photocatalytic H₂ generation. Coupling TiO₂ with another semiconductor such as CuO could modify and improve its photocatalytic activities (Ni, Leung et al. 2007, Chen, Shen et al. 2010). Significant enhancement of photocatalytic H₂ generation compared to the commercial P25 could be attained and was reported by our group (Xu and Sun 2009). Besides modifying the TiO₂ optical property, CuO also enhances the separation of photogenerated electrons and holes due to the TiO₂/CuO heterojunctions (Xu and Sun 2009, Xu, Du et al. 2011). However, photocatalytical nanoparticles tend to form aggregates which serve as recombination centers for the photogenerated electrons and holes (Choi, Kim et al. 2010), thus reducing the photocatalytic efficiency. On the other hand, TiO₂ nanofibers could offer a better alternative as it demonstrated higher photocatalytic activity than TiO₂ nanoparticles owing to its intrinsic properties such as: (1) one-dimensional long structure promoting charge transfer (Li and Xia 2004); (2) high porosity and large surface area enhancing mass transfer and light utilization rate; and (3) lower tendency to form aggregates that impedes the recombination of photogenerated electrons and holes (Choi, Kim et al. 2010). Nanofibers can be synthesized via several routes such as the hydrothermal method, sol-gel method, and electrospinning (Bian, Yu et al. 2007, Liu, Sun et al. 2007, Lin, Chao et al. 2008). Comparatively, electrospinning is the simplest and most inexpensive method as it does not require large amount of corrosive chemicals, high temperature, and complex synthesis steps (Dzenis 2004, Li, McCann et al. 2006). It offers a versatile route to tune and control the morphology and chemical composition of nanomaterials by varying electrospinning process parameters such as voltage, precursor solution concentration, flow rate, and humidity (Li, McCann et al. 2006). Recently, our group has reported a novel fully-exposed side-by-side bicomponent TiO₂/SnO₂ nanofibers obtained from electrospinning. This bicomponent TiO₂/SnO₂ nanofibers

exhibited excellent photocatalytic activity as a result of its nanofibrous morphology and special heterojunction structure which retard the recombination of photogenerated electrons and holes (Liu, Sun et al. 2007). However, the benefit from the heterojunction was limited only to the central joint where both TiO_2 and SnO_2 components were in contact on this nanofiber. Zhang et al. (2010) has fabricated electrospun ZnO/SnO_2 composite nanofibers with high porosity and enhanced specific surface (Zhang, Shao et al. 2010). Following this, both Hwang et al. (2011) (Hwang, Kim et al. 2011) and Lee et al. (2012) (Lee, Bai et al. 2012) have successfully fabricated $\text{TiO}_2/\text{SnO}_2$ composite nanofiber via electrospinning a precursor solution with homogeneous distribution of Ti and Sn. Despite the similar synthesis method employed and same chemical composite system with similar morphology, both of the $\text{TiO}_2/\text{SnO}_2$ composite nanofibers differed significantly in term of porosity, surface area, and light utilization which could influence the subsequent photocatalytic performance and application. These differences were likely attributed to the different raw materials used in the precursor solution. These studies have suggested that the facile electrospinning method has high potential and vast room for innovation in fabricating highly efficient photocatalyst of different composite system.

Despite its simplicity, the exploration of electrospun TiO_2 and its composite nanofibers is still relatively scarce (Sigmund, Yuh et al. 2006, Thavasi, Singh et al. 2008) and has been limited in particular for photocatalytic H_2 production from industrial wastewater. In view of its potential over other synthesis method, more dedicated research should focus on exploiting electrospinning for attaining a more viable TiO_2 photocatalytic H_2 and clean water generation from wastewater. Furthermore, electrospun TiO_2 nanofibers have been demonstrated to exhibit higher H_2 generation from methanol solution than that by TiO_2 nanofibers synthesized via hydrothermal method (Chuangchote, Jitputti et al. 2009). Continuous effort is necessary to identify, design and overcome the limitation of TiO_2 photocatalysts via electrospinning for use in wastewater in particular, to generate H_2 and reclaim clean water simultaneously. This would reinforce the environmental prospect and viability of photocatalytic H_2 generation over TiO_2 .

1.2 Research Approach and Hypothesis

The following approaches or opportunities will be explored in stages to overcome the identified challenges or limitation in photocatalytic H₂ generation from water, and to enhance its environmental prospect:

1. The usability of TiO₂ nanofibers for photocatalytic treatment of a wastewater will be explored first. The potential of integrating the merits of one-dimensional (1D) TiO₂ nanofibers with the nature of copper(II)-ethylene diamine tetra acetic acid (Cu-EDTA) waste water to cogenerate H₂ and clean water via photocatalysis, will be investigated for the first time. Electrospinning is chosen as a simpler synthesis method compared to the conventionally used hydrothermal method which entails more steps and corrosive chemicals. Furthermore, owing to its superior properties such as: (1) high porosity and long aspect ratio (Choi, Kim et al. 2010) which would enhance adsorption and uniform dispersion of reactants, and (2) low aggregation tendency which facilitate separation and reusability of the photocatalysts as well as reduce recombination of photogenerated charges. (Choi, Kim et al. 2010), 1D TiO₂ nanofibers may facilitate direct reclamation of the used TiO₂ photocatalyst with Cu deposited on it. The reclaimed composite photocatalysts may be re-usable efficiently for other photocatalytic application. Meantime, the use of Cu-EDTA will eliminate the need of methanol addition. Since it is easily available from the industry, Cu-EDTA offers an avenue to generate H₂ more sustainably.
2. The fabrication of TiO₂ composite nanofibers in just one step electrospinning will be undertaken. Even though TiO₂ composite nanofibers can be obtained easily by electrospinning multicomponent mixtures (Lu, Wang et al. 2009), the key challenge is to explore two or more of chemicals which are miscible, homogeneous, and stable in the preparation of the precursor solution since it could determine the properties of the electrospun nanofibers. Meanwhile, since there has not been any report on H₂

generation potential over TiO₂/CuO nanofibers (Chattopadhyay, Rok Kim et al. 2008, Sasikala, Sudarsan et al. 2008, Sasikala, Shirole et al. 2009), we hypothesized that a new morphology of TiO₂/CuO composite nanofibers should yield higher photocatalytic H₂ generation compared to their nanoparticle counterparts, the pristine TiO₂ nanofiber and the commercial P25.

3. The synthesized TiO₂ composite nanofibers will be used for different model organic pollutant as sacrificial reagent to investigate its application potential. The prospect is to convert waste water into resources, through which double environmental benefits can be reaped as organic pollutant can be removed and H₂ gas can be produced. Besides saving the cost of adding methanol (which is a fuel source itself) to the process, this also serves to determine its realistic usability over a wide range of waste water streams generated from the current major industries. It provides an avenue for water reuse which minimizes freshwater demand from the industry of concerned. The study on integrating pollutant decomposition and H₂ production is still lacking despite the encouraging results from the open literature. Related process mechanism and theory for simultaneous photocatalytic H₂ generation and organic pollutant removal in waste water will also be investigated.
4. The ability of the as-synthesized photocatalysts to function within the visible light range of the solar spectrum will be investigated and compared with its performance under UV-visible irradiation. Its ability to perform in the visible light range will definitely add more value to the novel nanomaterials and render it more attractive for a renewable and sustainable energy and clean water production. It is hypothesized that the composite nanofibers would be able to harvest visible light for photocatalytic H₂ generation due to red-shifting of their optical properties.

1.3 Objective and Scope

The synthesis and potential of TiO₂ composite nanofibers will be explored by employing electrospinning method, which is both simple and still young in the research and development for photocatalytic H₂ and clean water co-generation from waste water. Electrospun TiO₂ nanofibers will first be explored for its photocatalytic H₂ generation efficiency, followed by the design, synthesis, and enhancement of physicochemical properties of TiO₂ composite nanofibers.

The objectives of this study are as follows:

1. To investigate the potential of electrospun TiO₂ nanofibers for photocatalytic H₂ and clean water generation from Cu-EDTA waste water, complete with the revelation of the process mechanism.
2. To reclaim, characterize and investigate the application as well as the reusability potential of the used TiO₂ nanofibers from (1) above.
3. To synthesize and characterize novel TiO₂/CuO composite nanofibers with innovative chemical and physical properties via electrospinning a new composite mixture of precursor solution.
4. To investigate and compare the feasibility of TiO₂/CuO composite nanofibers from (2) and (3) to co-generate H₂ and clean water from some major industrial waste waters (dye AO7 and glycerol) through photocatalysis under UV-visible and visible lights irradiation.
5. To reveal the fundamental in-sight on how the main physicochemical properties of TiO₂/CuO composite would govern the photocatalytic H₂ and clean water co-generation.
6. To optimize TiO₂/CuO composite nanofibers

Simplicity and environmental sustainability are the two main keys driving this study. In line with this, the focus of this study is to enhance the photochemical properties of TiO₂ photocatalyst. It entails exclusively novel concept demonstrations between selected pollutants of concern and electrospun TiO₂ nanofibers or TiO₂ composite nanofibers for the first time, to generate H₂ and degrade pollutant simultaneously.

Hence, wastewater in this part of study assumed an ideal matrix where only the pollutant of concern such as Cu-EDTA, dye AO7, and glycerol, are present in their respective solution because this will be a preliminary study to first check (1) the possible use of TiO₂ nanofibers to generate H₂, decompose Cu-EDTA and reclaim composite materials; and (2) the possible use of composites synthesized herein to decompose AO7 and glycerol and generate H₂ concurrently. The use of real wastewater from the industry would not be considered as the possible presence of other contaminants in the real wastewater matrix and their probable effects (such as photocatalysts poisoning) on the final outcome is not part of the scopes at this initial research stage. Since synthetic wastewater containing only the selected pollutant of concern will be prepared in the lab for this study, the phrase "clean water production" in this study will refer to cleaner water which has lower degree of contamination with reference to the pollutant of concern. Nevertheless, the in-sights of the effect of other contaminants in the real wastewater are crucial, and should be included as this research advances positively in the future, if a more realistic progress relative to the technological readiness scale is desired.

1.4 Organization of thesis

This thesis comprises eight distinctive chapters.

Chapter One gives a brief introduction to the research background and its significance, the potential approaches which will be researched in this study, objectives and scope, and the organization of this thesis.

Chapter Two covers the literature reviews on the current research trend and challenges in photocatalytic H₂ production over TiO₂-based photocatalysts; as well as the potential and opportunities of the emerging nanosized photocatalysts in curbing the environmental sustainability issue, in particular nanofibers.

Chapter Three describes the materials used and methodologies employed in this study.

Chapter Four to Chapter Seven presents the results and discussions of this study. Chapter Four focuses on the feasibility study of electrospun 1D TiO₂ nanofibers to co-generate H₂ and clean water from Cu-EDTA waste water via photocatalysis. Characterization, prospective application and stability of the reclaimed TiO₂ nanofibers will be discussed. The mechanism of the entire process will be unravelled to bridge the research gap.

Chapter Five analyzes and discusses the characterization and basic application results obtained from the TiO₂ composite nanofibers synthesized through one-step electrospinning of innovative precursor solution.

Chapter Six discusses the photocatalytic efficiency and application potential of TiO₂ composite nanofibers (synthesized from both the reclaimed TiO₂ and the innovative precursor solution) in some industrial waste waters, under both UV-visible and visible light irradiation.

Chapter Seven systematically presents the fundamental relationship between the physicochemical properties of TiO₂ composite nanofibers and their photocatalytic efficiency.

Chapter Eight concludes the scientific achievement of this study and lays out recommendation for future advancement.

CHAPTER 2 LITERATURE REVIEW

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2.1 World crisis – Energy and Environment

Energy and environment are two top global problems today (Hightower and Pierce 2008). Owing to the burgeoning of worldwide industrialization and population growth, the conventional energy resources (coal, natural gas, petroleum, etc.) have been depleted at an alarming rate (Schloegl 2008). Global energy consumption is

expected to grow by 50% by 2030 (Hightower and Pierce 2008). The world reserves are predicted to last us another 30-40 years for oil and natural gas and 400-450 years for coal (Getoff 1990, Liu, Burghaus et al. 2010). Furthermore, the consumption of fossil fuels presents the threat of climate change due to the air emission of green house gases such as CO₂, NO₂ and CH₄ (Schloegl 2008, Chen, Shen et al. 2010). Climate change is also associated with the risk of reducing freshwater supply and its quality owing to alterations of precipitation patterns and evaporation rates from the rising atmospheric temperature (Lee, Bai et al. 2012). In response to the pressing global warming issue from the utilization of fossil fuel, hydrogen (H₂) as an ideal clean energy source has attracted large attention by researchers (Zou, Ye et al. 2001). H₂ is a very attractive fuel source due to a few attributes which include: (1) it can be derived from a variety of sources such as fossil fuels (natural gas, coal, petroleum), biomass and water (Conte, Iacobazzi et al. 2001, Chen, Shen et al. 2010), (2) upon production, it can be easily stored for later consumption, and (3) its production and utilization can be emission-free thus helps to address the air pollution and climate change issues (Conte, Iacobazzi et al. 2001).

2.2 Technologies for H₂ generation

2.2.1 General Overview of Technologies for H₂ Generation and Significance of Photocatalytic H₂ Production

H₂ may be produced via various technologies. Among the extensively researched methods are the electrolysis of water, steam reformation of methane, reformation of coal through gasification, biological processes using microorganisms, photoelectrochemical cell, and photocatalytic water splitting under sacrificial condition. Electrolysis of water entails high operation cost at large scales due to its electricity requirement, let alone the expensive capital cost. Steam methane reforming is also not sustainable as it requires the finite natural gas as feedstock and it generates CO₂ as the by-product. Although an additional process step for CO₂ sequestration is possible to address the CO₂ emission, the large portion of CO₂ produced in the gaseous product remains the source of the major green house gas emission, estimated to be around 78% of the overall global warming contribution

(Dunn 2002). Furthermore, the necessary sequestration process requires large amount of electricity which will accelerate the depletion of the fossil fuel. Likewise, coal gasification also consumes unsustainable coal feed and poses the concern of CO₂ production and need for sequestration. Meanwhile, biological H₂ production entails strict and cumbersome operational control for the survival of the highly sensitive microorganism and low H₂ production rate.

On the other hand, the principle of photoelectrochemical cell and photocatalytic water splitting processes is based on the photosynthesis process by the living plants which split water to produce H₂ upon irradiation of the sunlight (Kudo and Miseki 2009). Their operation requires only suitable photocatalysts which can be excited by photon from a solar radiation, which is free and inexhaustible. Both these processes are CO₂-free production technologies, thus are good pathways to sustainable clean energy production (Ashokkumar 1998, Kudo and Miseki 2009, Chen, Shen et al. 2010). Due to simplicity and higher advantageous for large scale application (Kudo and Miseki 2009), powdered photocatalysts systems will be considered in this study. Although the photon energy conversion via powdered photocatalysts is not at the stage of practical use, its research for H₂ generation is advancing and new photocatalyst materials is being discovered and reported one after another.

2.2.2 Basic Mechanism of Photocatalytic Water Splitting

The fundamental principle of a semiconductor-based photocatalytic water splitting process for H₂ production is as shown in Fig. 2.1. A photocatalyst usually consists of a valence band (VB) and a conduction band (CB). Upon absorption of photons with energy larger than that of the photocatalysts' band gap, electrons and holes will be formed in the CB and VB, respectively. Then, the photogenerated electrons and holes will be separated and migrate to the surface reaction sites. This process takes advantage on photocatalysts with high quality crystallinity (low defectivity) and smaller particle size which minimize the recombination rate of the photogenerated charge and facilitate the migration of electrons and holes to the surface reaction

sites due to the shorter travel distance, respectively (Kudo and Miseki 2009). At the reaction sites, water molecules are reduced by the electrons to form H_2 and are oxidized by the holes to form O_2 . A minimum theoretical band gap of 1.23 eV is required for water splitting to take place. Figure 2.2 illustrates an overview of the main processes in photocatalytic water splitting from charges generation through their utilization (Kudo and Miseki 2009). For H_2 generation to happen, the CB of TiO_2 must be more electronegative than the H_2O reduction potential as shown in Fig. 2.3

Figure 2.1 Fundamental principle of semiconductor-based photocatalytic water splitting for hydrogen production (Chen, Shen et al. 2010)

Figure 2.2 Main processes in photocatalytic water splitting (Kudo and Miseki 2009)

Figure 2.3 Relationship between band structure and redox potentials of H_2 generation from H_2O (Kudo and Miseki 2009)

One major problem in water splitting process is the possible recombination of H_2 and O_2 to produce H_2O thus resulting in low H_2 yield. To overcome this, sacrificial reagent can be added to the system as electron donor in place of pure water. Consequently, the O_2 formation will not take place. Instead, the electron donor will be oxidized by the holes (Kudo and Miseki 2009). The understanding of the basic main processes reveals that a highly efficient photocatalytic H_2 production requires the availability of photocatalysts which must exhibit all the basic criteria as follows:

- Appropriate band gap for efficient solar energy harvesting,

- High crystallinity and small particle size, and
- Large surface area and active sites

2.3 TiO₂ Photocatalysts for Photocatalytic H₂ Generation

2.3.1 Introduction to TiO₂

Among the various photocatalysts, TiO₂ semiconductor is widely-studied due to its non-toxicity, chemical stability, high efficiency and low-cost (Banerjee 2011). It has found various applications such as in consumer products like sunscreens (Popov, Priezzhev et al. 2005, Jaroenworarluck, Sunsaneeyametha et al. 2006, Serpone, Dondi et al. 2007, Nohynek, Dufour et al. 2008) and paints (Maggos, Bartzis et al. 2007, Schmid and Riediker 2008) to name a few. Ability of TiO₂ to degrade organic pollutants in water was first discovered in 1996 (Bekböt and Özkösem 1996, Bekböt and Balcioglu 1996). Meanwhile, the most significant discovery of TiO₂ for water splitting on a TiO₂ electrode under ultraviolet light was first reported by Fujishima and Honda in 1972 (Fujishima and Honda 1972). Following this, exponential growth of research started to take place especially on the exploitation of TiO₂ photocatalysis in energy resolution for H₂ production (Gupta and Tripathi 2011) and environmental remediation such as air purification (Peral and Ollis 1992, Hager and Bauer 1999, Fujishima, Rao et al. 2000, Li, Li et al. 2005), water treatment (Byrne, Eggins et al. 1998, Li and Li 2001, Neppolian, Choi et al. 2002), and antimicrobial coating or disinfection (Fu, Vary et al. 2005, Page, Palgrave et al. 2007), to name a few. The chemical reactions during photocatalysis involving TiO₂ photocatalyst have been widely postulated as a series of possible oxidation and reduction equations as follows (Fujishima and Honda 1972, Fujihira, Satoh et al. 1981, Anna and Jerzy 2005, Chong, Jin et al. 2010):

In the presence of oxygen, peroxide radical could be generated to generate hydrogen peroxide (H₂O₂) which adds on to the formation of hydroxide radical. Postulated possible equations are as follows:

Hydroxide radical (OH[·]) and other radical species such as superoxides radical (O₂^{·-}) and hydroperoxyl radical (HO₂[·]), termed as the reactive oxidant species (ROS), could mediate oxidation reactions during photocatalysis.

In the absence of electron or hole scavenger, both electron and hole may recombine rapidly while releasing heat energy concurrently (Chong, Jin et al. 2010). In the presence of organic pollutants (R-H) which acts as the hole scavenger, photo-degradation of R-H may be possibly represented as follows:

(photo-degradation mediated by OH[·])

(photo-degradation initiated by h⁺)

In the presence of electron scavenger (A), the following reaction may take place:

The overall photocatalysis reaction entails five independent steps as follows (Chong, Jin et al. 2010):

1. Mass transfer of the reactants (either organic pollutant or electron scavenger) from the bulk solution to the surface of TiO_2 photocatalyst.
2. Adsorption of reactants onto the surface of activated TiO_2 .
3. Photocatalysis of the adsorbed phase on the surface of TiO_2 .
4. Desorption of the intermediate(s) from TiO_2 surface.
5. Mass transfer of the intermediate(s) from the interface region into the bulk solution.

Adsorption is the pre-requisite to ensure successful photo-degradation. Steps 1 and 5 are fast happening than Steps 2, 3, and 4, all in nanoseconds (Hoffmann, Martin et al. 1995). Therefore, the concentration difference of the reactants on the solid surface and bulk solution are negligible; while the later three steps are the rate determining steps depending on the efficiency of the TiO_2 photocatalyst.

2.3.2 Limitation of TiO_2

Despite its great potential, TiO_2 possesses two major inherent limitations: (1) wide band gap of 3.2 eV thus can absorb and utilize ~3% of the solar radiation (Gupta and Tripathi 2011), and (2) rapid recombination of photogenerated electrons and holes pairs. As a consequence it has low photocatalytic efficiency which deters its practical application (Banerjee 2011, Gupta and Tripathi 2011). In view of this, a lot of research has been devoted to modify and improve optical TiO_2 properties for enhanced photocatalysis (Ni, Leung et al. 2007). On top of this, a synergistic combination of size, morphologies, porosity, surface area, and crystalline properties also determine the net photoactivity of TiO_2 (Liu, Piao et al. 2010). Meanwhile, the efficiency of TiO_2 could be adversely affected by intermediate by-products which were produced during photocatalysis, or heteroatom contaminant containing N,S,P, or Si atom which could be present in the medium of reaction; owing to the deposition of the respective compounds on the photocatalysts upon photo-oxidation. This phenomena, usually termed as photocatalysts poisoning, has been reported to adversely affect activity of TiO_2 thus reducing its reusability potential if the poisoning is completely irreversible (Peral and Ollis 1997, Dutta, Parsons et al.

2009). On the other hand, a reversible deactivation could be overcome via a heat treatment in the air {Peral, 1997 #580}.

2.4 Overcoming Challenges in TiO₂ Photocatalytic Water Splitting

2.4.1 Addition of Sacrificial Reagent

Sacrificial reagent can be added into the reaction solution to increase the efficiency of photocatalytic H₂ generation. It reacts as an electron donor (or photogenerated hole scavenger) thus enriches the photogenerated electrons in a photocatalyst for enhanced H₂ generation (Fig. 2.4(a)) (Kudo and Miseki 2009).

Figure 2.4 (a) Photocatalytic H₂ generation in the presence of sacrificial reagents (Kudo and Miseki 2009) and (b) Generic representation of photocatalysis over TiO₂ to degrade organic pollutant and generate H₂ simultaneously (Litter 1999)

Consequently, recombination of H₂ and O₂ are retarded as photogenerated hole is consumed to oxidize the sacrificial reagent. Meanwhile, ROS could oxidize the sacrificial reagent as well. Sacrificial reagent can be inorganic or organic (Chen, Shen et al. 2010). Alcohols (such as methanol, ethanol, isopropanol, etc.), aldehydes (such as formaldehyde, acetaldehyde, etc.), H₂S, I⁻, Br⁻, CN⁻, and S²⁻

/SO₃²⁻ have been reported to enhance photocatalytic reaction (Wu and Lee 2004, Xu and Sun 2009, Chen, Shen et al. 2010, Daskalaki, Antoniadou et al. 2010, Lianos 2011) Chemical reactions involving S²⁻/SO₃²⁻ and methanol (CH₃OH) as example of inorganic and organic sacrificial reagent respectively were postulated as follows (Chen, Shen et al. 2010):

S²⁻/SO₃²⁻:

(S₂O₃²⁻ can be further oxidized to SO₃²⁻ and SO₄²⁻)

CH₃OH:

Overall reaction for methanol: CH₃OH + TiO₂ + hν → TiO₂ + CO₂ + H₂O

One attractive approach which has drawn research attention is the use of organic pollutant which is readily available in the industrial organic wastewaters such as EDTA (Kim and Choi 2010), phenol (Kim and Choi 2010), glycerol (Yu and Ran 2011) and azo-dye (Patsoura, Kondarides et al. 2006). Organic pollutants in the waste water present an attractive alternative for exploitation because (1) it is readily available from industries, and (2) it needs to be decomposed before safe discharge

into the environment. Figure 2.4 (b) shows a generic representation of how organic pollutant degradation as well as H_2 generation could take place concurrently during a photocatalytic reaction. D is an electron donor (hole scavenger), which could represent organic pollutant such as azo-dye, EDTA, glycerol and other pollutant degradable via photocatalytic oxidation by the holes (h^+) or ROS (generated by h^+) as discussed earlier, thus preventing the water oxidation into O_2 (Patsoura, Kondarides et al. 2007). Upon absorption of photon with energy higher than the band gap energy of a photocatalyst, E_g , h^+ and e^- will be generated in VB and CB, respectively. Thermodynamically, D can be oxidized (degraded) by h^+ if the VB is more electropositive than the oxidation potential for D (Litter 1999). Meanwhile, A is an electron acceptor, possibly representing H_2O which eventually will be reduced to form H_2 if the CB is more electronegative than H_2O reduction potential as discussed earlier. Both A and D are usually adsorbed or close to the surface of the photocatalyst.

Carbohydrates such as sugar, starch and cellulose has been used for conversion into H_2 via photocatalytic process over $RuO_2/TiO_2/Pt$ photocatalyst (Kawai and Sakata 1980). Glycerol has been used as the sacrificial reagent for an efficient H_2 production where its decomposition was achieved simultaneously over CuO -modified TiO_2 (Yu, Hai et al. 2011). A simultaneous H_2 production and degradation of common waste products from biomass processing industries such as acetic acid, ethanol, propanol, butanol, formic acid, and acetaldehyde; has also been reported over Pt -based photocatalysts (Sakata, Kawai et al. 1984, Cortright, Davda et al. 2002, Patsoura, Kondarides et al. 2007, Zheng, Wei et al. 2009). In a separate study, use of ethanol as sacrificial reagent for photocatalytic degradation and simultaneous production of H_2 has been reported using $Pt/CdS/TiO_2$ photocatalyst (Daskalaki, Antoniadou et al. 2010). Meanwhile, the photocatalytic degradation of azo-dyes into CO_2 and inorganic ions over $Pt-TiO_2$ photocatalyst has been shown to enhance the photocatalytic H_2 production in the single process (Patsoura, Kondarides et al. 2006). Within our group, we have reported successful fabrication of TiO_2 nanotube for simultaneous photocatalytic H_2 production and Cu^{2+} removal (Xu, Ng et al. 2011).

Such bifunctional photocatalytic systems not only could generate H_2 to possibly minimize the energy demand and cost, but also a cleaner water concomitantly thus providing an avenue for water reuse which minimizes freshwater demand from the industry of concerned. This in turn could help ameliorate both the looming energy crisis and water scarcity problem in years to come. Nonetheless, with the booming research to modify and design more efficient photocatalysts in the recent years, much work is still required to expand the knowledge bank for deeper understanding on the applicability of each photocatalysts for the broad range of waste water (Ni, Leung et al. 2007). This is because each photocatalyst synthesized is unique in structure, energy utilization and conversion efficiency, morphology, surface properties (surface area and reactive sites), and porosity. The study of concurrent organic waste water oxidation and H_2 generation over TiO_2 photocatalysis is in general still scarce in terms of design for its used in different waste water, breadth of pollutant type, and depth of a study. Usually, one photocatalyst may be efficient in photocatalytic organic oxidation but not for photocatalytic H_2 production and vice versa. In addition, each may be usable in one type wastewater but others may be usable for more or none. Each may exhibit different mechanism and reaction path, thus requires different optimum operating parameters (pH, photocatalysts concentration, etc.) to function. Hence, research should focus on identifying and/or designing suitable TiO_2 photocatalyst for application in industrial wastewater while finding new pollutant alternatives to eliminate the dependence on useful chemicals.

An interesting study within our group was the use of Cu^{2+} - methanol aqueous solution to demonstrate the generation of H_2 and removal of Cu^{2+} over TiO_2 nanotube (TNT) (Xu, Du et al. 2011). In this study, Cu^{2+} was removed from the solution and photo-deposited onto TNT. H_2 generation was greatly enhanced owing to the role of Cu as co-catalyst. If a waste water stream comprising similar nature as the Cu^{2+} - methanol aqueous solution could be identified i.e. organometallic, it may offer an avenue to not only generate H_2 and produce clean water, but also recover precious metal simultaneously over TiO_2 photocatalysis in a green manner.

Copper(II)- ethylene diamine tetra acetic acid (Cu-EDTA) is a type of organometallic wastewater usually generated from textile, electroplating, and nuclear industries (Cho, Shin et al. 2006, Park, Jung et al. 2006). It is very stable over a wide range of pH and highly resistant to degradation. Cu-EDTA wastewater must be treated before discharge, because its persistence in the environment can be detrimental to life as it increases the mobility of Cu elements which can be toxic at high concentration (Nybroe, Brandt et al. 2008). Unlike the conventional physical-chemical and biological treatments which entail complex operation and maintenance procedures, high resources demand, as well as treatment efficiency and post-treatment challenges (Chang 1995, Chung and Rho 1999, Chaudhary, Donaldson et al. 2000, Kim, Lee et al. 2003, Wu, Wang et al. 2013), photocatalytic treatment of Cu-EDTA may represents a simpler and more promising technology to treat Cu-EDTA as (1) it taps into the clean and renewable solar energy, (2) it does not require additional chemicals, and (3) it does not generate secondary pollutant. Few reports have demonstrated the promising ability of TiO₂ P25 nanoparticles to oxidize EDTA from Cu-EDTA and consequently adsorb the released Cu under solar irradiation thus producing clean water (Madden, Datye et al. 1997, Yang and Davis 2000, Cho, Shin et al. 2006). Meanwhile, past research have showed that Cu was a good co-catalyst and candidate to modify TiO₂ thus enhancing its photocatalytic H₂ generation significantly (Wu and Lee 2004, Xu and Sun 2009, Xu, Du et al. 2011, Yu and Ran 2011). Hence, in principle, the Cu, following its release and adsorption onto the TiO₂ during photocatalytic oxidation (PCO) of Cu-EDTA, would facilitate an efficient H₂ generation. Nevertheless, the extent of research remains limited with possible sought-after opportunities to enhance the viability of photocatalytic treatment of Cu-EDTA over TiO₂, one of which is to use it as a sacrificial reagent for H₂ generation. While EDTA solution itself has been proven to enhance H₂ generation (Sabaté, Cervera-March et al. 1990, Ni, Leung et al. 2007, Kim and Choi 2010, Zhou, Qu et al. 2012), no study on even possible photocatalytic H₂ generation from Cu-EDTA was ever reported to date. Meanwhile, Cu could be recovered from the used photocatalysts using acid extraction. (Rhoads and Davis 2004) Despite the benefits of concurrent organic degradation and Cu recovery which produce clean water, environmental challenges remain where the post-treatment and complexity of

the recovery steps entail intensive use of chemicals, high resources demand and secondary wastewater generation. The challenge is further compounded as exploration to recover the deposited Cu via a greener approach seems to be very few. If the used photocatalyst with Cu deposited on it is reclaimable and reusable, this may open a door to another synthesis route for functional TiO₂ composite. Ng, Ikeda et al. (2012) (Ng, Ikeda et al. 2012) has reported the potential use of photoreduction via photocatalysis as one of the route to synthesize carbon-based nanomaterials.

2.4.2 Improving Photocatalytic Efficiency of TiO₂

With a view to developing TiO₂ nanomaterials with enhanced photocatalysis efficiency, extensive studies have been conducted which largely focus on the following objectives:

- (a) Improvement of optical activity - Enhance the absorption of light and extend utilization of solar irradiation from UV to Visible light region

Commonly employed approaches are:

- chemical modification (Khan, Al-Shahry et al. 2002, Chen and Mao 2007, Kudo and Miseki 2009) via doping of TiO₂ with metal ion such as Fe³⁺, Mo⁵⁺, Ru³⁺, Cr³⁺, Mn²⁺, etc (Choi, Termin et al. 1994, Litter 1999, Dvoranová, Brezová et al. 2002), and non-metal ions such B, C, N, etc (Gandhe and Fernandes 2005, Shen, Wu et al. 2006, Chen, Wang et al. 2008, Górska, Zaleska et al. 2009, Nie, Xu et al. 2011, Xue, Zhang et al. 2011). As illustrated in Fig. 2.5(a), the incorporation of metal or non-metal ions into TiO₂ lattice will create an impurity energy level which is an energy gap that does not form a complete band (Kudo and Miseki 2009). This results in a narrower thus lower energy requirement to induce electrons and holes pairs generation. Meanwhile, the addition of ions could also create new VB (or an electron donor level) in the band gap of TiO₂ (Fig. 2.5(b)) which enable it to utilize the wider fraction of solar radiation i.e. visible region by creating a new narrower band gap (Chen and Mao 2007). Figure 2.6 shows the example of different new VB depending on the type of metal used. Generally, the CB of TiO₂ should not be further lowered to attain a smaller band gap or energy gap so as to ensure H₂ could

be generated via photo-reduction. If CB has a lower reduction potential than the H_2O reduction potential, H_2 could not be generated.

Figure 2.5 (a) cation or anion doping which creates an impurity energy level (DL) within the forbidden bandgap of TiO_2 , (b) valence band modification which forms a new VB with higher top, and (c) solid solution formation which forms new couple of VB and CB whose bandgap is between those of TiO_2 (Zhu and Zäch 2009)

Figure 2.6 Metal-doped TiO_2 with new VB level under photoexcitation by visible light: (a) $\text{Ti}_{1-x}\text{V}_x\text{O}_2$; (b) $\text{Ti}_{1-x}\text{Fe}_x\text{O}_2$; (c) $\text{Ti}_{1-x}\text{Cr}_x\text{O}_2$ (Chen and Mao 2007)

- Dye-sensitization, metal/non-metal ion codoping, or noble metal addition are other available routes to chemical modification which has been shown to shift the TiO_2 's photoresponse into visible light range hence enhancing its solar light utilization (Dhanalakshmi, Latha et al. 2001, Song, Zhou et al. 2008, Kim, Lee et al. 2009, Gupta and Tripathi 2011). Figure 2.7 illustrates the general principle of how dye-sensitization works in facilitating photocatalytic H_2 generation. Adsorption of dye molecules is the pre-requisite before the initiation of enhancement reaction. Upon absorption of photon, adsorbed dye will be excited, inject electrons into the CB of TiO_2 for reduction of H_2O into H_2 . In this process, dye is regenerable, where

it will be oxidized and then reduced again. Ruthenium (Ru) complex dyes, polypyridine complexes, alizarine with metal centers such as Pt(II), Co(II) and Cr(III), metal free dyes (prophine, xanthene, Rhodamine B, Eosin Blue) have been used as sensitizers (Chen, Shen et al. 2010). Higher H₂ generation activity may be obtained in the presence of electron donor such as ethylene diamine tetra acetic acid (EDTA) (Chen, Shen et al. 2010).

Figure 2.7 Basic principle of dye-sensitized photocatalytic H₂ production from water (Chen, Shen et al. 2010)

Meanwhile, co-doping can be done using metal (noble metal or transition metal) or non-metal (Kudo and Miseki 2009, Chen, Shen et al. 2010). Noble metals which have been commonly researched were Pt, Pd, Cu, Ag, Ru, Au and Rh, with Pt being the most popular.

- Coupling TiO₂ with another semiconductor of narrower band gap (which is sensitive to visible light) to form TiO₂-based composite semiconductor by visible light i.e. CdS (Wang, Sun et al. 2009, Chen, Shen et al. 2010, Banerjee 2011, Liu, Zhou et al. 2011). This is similar to the principle of dye-sensitization. Figure 2.8 illustrates a TiO₂/CdS heterojunction structure. Since the CB of CdS is more electronegative than that of TiO₂, its photogenerated electrons will be transferred to

the CB of TiO_2 upon absorption of visible light (Ni, Leung et al. 2007). Other heterojunctions which have been reported to have visible light absorption capability thus demonstrated photocatalytic H_2 generation enhancement include $\text{TiO}_2/\text{SrTiO}_3$ (Ng, Xu et al. 2010), TiO_2/CuO (Xu, Du et al. 2011), $\text{TiO}_2/\text{SnO}_2$ (Sasikala, Shirole et al. 2009), and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ (Chen, Shen et al. 2010).

Figure 2.8 CdS/ TiO_2 heterojunction - an example of coupling two semiconductors of narrow band gap and wide band gap each to enable activation under visible light irradiation (Chen, Shen et al. 2010)

(b) Enhance charge migration and separation of the photogenerated electron and hole pairs

In most cases, both enhancement in visible light sensitivity and charge separation would be attained concurrently because commonly employed approaches and modification principles are mostly similar to that adopted for improvement of optical property as discussed before:

- Coupling TiO_2 with another semiconductor such as SnO_2 have been reported to enhance charge migration and separation (Cao, Zhang et al. 2000, Liu, Sun et al. 2007, Zhang, Wu et al. 2009). The CB and VB of SnO_2 are lower than that of TiO_2 . This potential difference has made it possible for photogenerated electrons to migrate from TiO_2 's CB to SnO_2 's CB, while photogenerated holes will tend to migrate from SnO_2 's VB to TiO_2 's VB. This has thus resulted in lower recombination of the photogenerated electron and hole pairs. Our group has also worked on TiO_2/CuO nanoparticles and TiO_2/CuO nanotube using P25 as the

precursor for H_2 generation. Significant enhancement of photocatalytic H_2 generation was attained and reported. Besides modifying the TiO_2 optical property, CuO also enhances the separation of photogenerated electrons and holes due to the TiO_2/CuO heterojunctions (Fig.2.9) (Xu and Sun 2009, Xu, Du et al. 2011).

Figure 2.9 Charge transfer in TiO_2/CuO under UV-visible light irradiation (Xu, Du et al. 2011)

- Elemental doping (metal, non-metal, noble) such as by Ag^+ , Fe^{3+} , Eu^{3+} , Cu^{2+} , etc was also one common approach to minimize charge recombination rate (Yang, Lu et al. 2002, Arabatzis, Stergiopoulos et al. 2003, Xu, Ng et al. 2011). The elements act as electrons or holes trap which result in more efficient separation of the charge carriers (Fig. 2.10). Copper element is one of the most widely explored especially as a co-catalyst for enhancement in photocatalytic H_2 generation in the past years as it is relatively low-cost and abundant, compared to the expensive and rare noble metals such as Pt and Pd.

Figure 2.10 Basic principle of co-catalyst doping; lower charge recombination due to the transfer between host photocatalyst and Pt as co-catalyst (Chen, Shen et al. 2010)

- Modification of crystal structure. A good example is the presence of both anatase and rutile phase in TiO_2 nanomaterials which have been demonstrated to enhance the separation of the photogenerated electron and hole pairs than that with only anatase phase due to the energy level difference (Sun and Smirniotis 2003, Liu, Zhang et al. 2007, Gupta and Tripathi 2011). Liu et al. (2007) (Liu, Zhang et al. 2007) have synthesized TiO_2 photocatalysts with anatase and rutile and demonstrated a more efficient photocatalytic reaction owing to the synergistic effect between the two crystal structures which facilitated charge transfer from anatase to rutile as well as the absorption capability in the short-wavelength region of the UV-vis light spectrum.
- Combination of different TiO_2 modification methods have been adopted to design and create a more efficient photocatalyst (Ni, Leung et al. 2007). A reported example was the use of composite semiconductors as the host for metal doping (Li, Haneda et al. 2004). In view of this, $\text{TiO}_2/\text{SnO}_2$ composite nanomaterial, for example, could offer as a potential host or support semiconductor due to its high thermal and chemical stability (Ni, Leung et al. 2007, Chen, Shen et al. 2010). As discussed before, it also offers a more efficient separation of photogenerated electrons and holes (Ni, Leung et al. 2007). In addition, a few studies have also

reported that addition of SnO₂ into TiO₂ nanoparticles could promote UV-vis light absorption (Uchiyama and Imai 2005, Long, Dai et al. 2009), hence improving its photoresponse and photocatalytic activity. There are a lot of publications on the superiority of TiO₂/SnO₂ composite system over pristine TiO₂ for photocatalytic degradation of organic dyes (Vinodgopal, Bedja et al. 1996, Cao, Zhang et al. 2000, Hou, Yuan et al. 2007, Liu, Sun et al. 2007, Sasikala, Shirole et al. 2009, El-Maghraby 2010). A study on Fe-doped TiO₂/SnO₂ nanomaterials has showed to exhibit much higher photocatalytic activity than pristine TiO₂ and even TiO₂/SnO₂ due to the reinforced separation of photogenerated electrons and holes between the different phases of the heterojunctions (Zhang, Wu et al. 2010). Sasikala et al. (2008) has demonstrated that Eu-doped TiO₂/SnO₂ exhibited higher photocatalytic H₂ production in aqueous methanol compared to TiO₂/SnO₂ nanocomposite owing to the presence of defect levels in TiO₂ which has improved the light absorption (Sasikala, Sudarsan et al. 2008).

- Physical modification. A lot of research have been focused on designing, fabricating and improving photocatalysts including TiO₂, in the nano-range for the past decades (Fig. 2.11) (Zhu and Zäch 2009). This can also be termed as a type of physical modification in order to improve TiO₂ photocatalytic efficiency via modification of physical properties such as crystalline size or structure, morphology, specific surface area and porosity (Hernandez-Alonso, Fresno et al. 2009). Photocatalytic properties hence the efficiency of a nanomaterial is influenced by the synergy of morphology, dimensionality, crystalline phase, structure, composition, size, structure, and composition of the nanomaterial (Liu, Burghaus et al. 2010, Banerjee 2011, Ng, Pan et al. 2011). It has been claimed that the optical properties and energy transfer can be tuned base on their size, shape, composition (Liu, Burghaus et al. 2010). Crystal phase with low defects and low grain boundaries could retard the recombination rate of the photogenerated electrons and holes (Fig. 2.12) (Kudo and Miseki 2009). Small particle size promotes the migration of the photogenerated electrons and holes to the reaction sites on the surface of a photocatalyst owing to a shorter distance (Fig. 2.12) (Kudo and Miseki 2009).

Figure 2.11 The number of publications on (nano)photocatalytic H₂ production. The inset shows the fraction of publications on photocatalytic H₂ production dealing with nano-aspects. (Zhu and Zäch 2009)

Figure 2.12 Effects of particle size and boundary on photocatalytic activity (Kudo and Miseki 2009)

2.5 One-Dimensional (1-D) TiO₂ Nanomaterials

Nanotechnology plays a key role in the resolution of energy and environmental problem for the future (Schloegl 2008, Liu, Burghaus et al. 2010). Nanomaterials

exhibit inherent unique properties such as increased surface active sites and surface-to-volume ratio which facilitate the heterogeneous catalysis and inner interfaces which governs the charge transport properties (Chen and Mao 2007, Schloegl 2008). TiO₂-based nanoparticles (0-D) has spawned tremendous amount of research work on development of photocatalysts for application in the photocatalytic H₂ production and waste water treatment (El-Bahy, Ismail et al. 2009, Khataee, Vatanpour et al. 2009, Xu and Sun 2009, Gupta and Tripathi 2011) owing to its large specific surface area and rapid surface reaction (Ng, Pan et al. 2011). However, nanoparticles possess an inherent tendency to form aggregates which serve as recombination centers for the photogenerated electrons and holes (Choi, Kim et al. 2010, Pan, Sun et al. 2010). Commercial TiO₂ nanoparticles, P25, for example, have been reported to aggregate easily in the aqueous solution which reduced surface area and low separation efficiency of photogenerated electrons and holes pairs (Bai, Zhang et al. 2009). On the other hand, one-dimensional (1-D) nanomaterials such as nanotubes, nanowires, nanorod, etc. have been claimed to be more efficient and offers more stable platform for further development because of its unique morphology and high surface area to volume ratio (Banerjee 2011). TiO₂ nanofibers have been reported to show higher photocatalytic activity owing to its intrinsic properties such as: (1) one-dimensional long structure promoting charge transfer (Li and Xia 2004); (2) high porosity and large surface area enhancing mass transfer and light utilization rate; and (3) lower tendency to form aggregates that impedes the recombination of photogenerated electrons and holes (Zhu and Zäch 2009, Choi, Kim et al. 2010). Previously, our group has synthesized TiO₂/CuO nanotube and has attained significant enhancement of photocatalytic H₂ generation compared to P25 (Xu, Du et al. 2011, Xu, Ng et al. 2011) addressed by its increased surface area for enhanced mass transfer and interfacial charge transfer. Various other 1-D TiO₂-based composite such as nanowhiskers and nanofibers which exhibited enhanced photocatalytic performance compared to P25, have also been reported (Ng, Xu et al. 2010, Ng, Pan et al. 2011, Xu, Du et al. 2011, Xu, Ng et al. 2011).

1-D TiO₂ composite nanomaterials can be synthesized via different methods such as the hydrothermal (Yuan and Su 2004, Rhee, Lee et al. 2005, Li, Cao et al. 2011), sol-gel/polymerization (Sui, Rizkalla et al. 2005, Bian, Yu et al. 2007), solvothermal (Wang, Wen et al. 2006), direct oxidation i.e. anodization (Ng, Zhang et al. 2010) and electrospinning (Liu, Sun et al. 2007, Zhang, Wu et al. 2009), to name a few. Comparatively, electrospinning is the simplest and most inexpensive method (Dzenis 2004, Li, McCann et al. 2006). Other synthesis methods entail multiple steps and chemical solvents, high fabrication cost, and possible generation of secondary waste. Moreover, the ability to fabricate TiO₂ nanomaterials with good dispersion of elements, well-controlled sizes, shapes, porosities, crystalline phases, and structures via these methods remains a challenge which need to be tackled (Liu, Burghaus et al. 2010).

Electrospinning followed by high-temperature calcinations, among others, is the most facile and relatively inexpensive technique to produce 1-D nanofibers. It is claimed to be one of the powerful tools for fabricating 1-D nanomaterials in future (Lu, Wang et al. 2009) and thus garnering much attention recently. It is also a versatile method to tune and control the morphology and chemical composition of nanofibers (Li, McCann et al. 2006), making it a convenient and user-friendly tool to manipulate nanofibers synthesis. This can be easily achieved by varying electrospinning process parameters such as voltage, precursor solution chemical and concentration, flow rate, and humidity (Li and Xia 2003). In a study carried out by Chuangchote et al. (2009), electrospun nanofibers were shown to have better crystallinity quality i.e. 100% anatase which exhibit more efficient photocatalytic activity than those synthesized via other method i.e. anatase and titanate B by hydrothermal method (Jitputti, Suzuki et al. 2008, Chuangchote, Jitputti et al. 2009). Based on the vast literatures available, electrospinning has been not only a focus of academic study in the laboratory but is also being applied in a great many technological fields (Lu, Wang et al. 2009). Electrospun TiO₂ nanofibers have been demonstrated to exhibit higher H₂ generation from methanol solution than that by TiO₂ nanofibers synthesized via hydrothermal method (Chuangchote, Jitputti et al. 2009). Despite that, the studies on electrospun TiO₂ and its composite nanofibers

for simultaneous photocatalytic H_2 generation and waste water treatment are still at the infancy stage and thus need to be further investigated (Thavasi, Singh et al. 2008). The diversity of materials which can be used for direct electrospinning still requires a lot of study for expansion. More effort and collaboration are required to explore and exploit the best potential of electrospun nanofibers for energy and environmental application.

Recently, our group has reported an excellent photocatalytic oxidation under UV light by a novel fully-exposed side-by-side TiO_2/SnO_2 nanofibers from electrospinning (Fig. 2.13) (Liu, Sun et al. 2007). However, the benefit from the heterojunction was limited only to the central joint where both TiO_2 and SnO_2 components were in contact on this nanofiber (Fig. 2.13).

Figure 2.13 (a) and (b) SEM images of electrospun TiO_2/SnO_2 that were calcined at $500^\circ C$, (c) EDS analysis of a single nanofiber, and (d) XRD diffraction patterns for the TiO_2/SnO_2

Thereafter, Hwang et al (Hwang, Kim et al. 2011) reported the synthesis of SnO_2 -embedded TiO_2 nanofibers with enhanced contact area between TiO_2 and SnO_2 for organic photo-oxidation. However, there was no improvement on its porosity, surface area, and light utilization rate which also dictate the photocatalytic reaction.

Therefore, researchers are still searching for ways to fabricate $\text{TiO}_2/\text{SnO}_2$ and other TiO_2 composite nanofibers encompassing benefits of long nanofibrous morphology, modified electronic properties, high dispersion of heterojunctions, and enhanced porosity, surface area, and light absorption. Following this, Lee et al. (2012) (Lee, Bai et al. 2012) successfully fabricated $\text{TiO}_2/\text{SnO}_2$ composite nanofiber via electrospinning an innovative precursor solution with homogeneous distribution of Ti and Sn. This $\text{TiO}_2/\text{SnO}_2$ composite nanofiber exhibited excellent physicochemical properties enhancement such as red-shift of light absorbance, smaller crystal size, enhanced mesoporosity and specific surface area; which promote photocatalytic H_2 from methanol. Despite the similar synthesis method employed and same chemical composite system with similar morphology for both Hwang et al (Hwang, Kim et al. 2011) and Lee et al. (2012) (Lee, Bai et al. 2012), both of the $\text{TiO}_2/\text{SnO}_2$ composite nanofibers differed significantly in term of porosity, surface area, and light utilization which could influence the subsequent photocatalytic performance and application. These differences were likely attributed to the different raw materials used in the precursor solution. These studies have thus suggested that the facile electrospinning method has high potential and vast room for innovation in fabricating highly efficient photocatalyst of different composite system. Functionally-improved TiO_2 composite nanofibers can be obtained easily by electrospinning multicomponent mixtures (Lu, Wang et al. 2009). Requiring only a high voltage supply, precursor solution of any metal alkoxides with the right surface tension, conductivity, and surface charge, could be electrospun to produce functional nanomaterials. Subsequent calcinations at high temperature could be employed to obtain the desired ceramic phase of the as-spun nanomaterials. The challenge is to obtain two or more precursors which are miscible, homogeneous, and stable. Hence, the diversity of materials which can be used for direct electrospinning still requires a lot of study for expansion.

2.6 Summary

Photocatalytic H_2 and clean water generation over TiO_2 nanofibers from wastewater remains a promising technology for alleviating the rising global environment and energy crisis. Enhancing the environmental viability may represent one good

approach to promote and motivate research utilizing TiO_2 photocatalysis, and eventually in the real field application in the future. Therefore, electrospinning and photocatalytic wastewater treatment are two key drivers in this research. More research is necessary to build on the fundamental science for using TiO_2 or TiO_2 -based composite nanofibers made from the facile electrospinning method. The diversity of materials which can be used for direct electrospinning still requires a lot of study for expansion. One area is undertaking more innovation in electrospinning method and experimental design to synthesize new TiO_2 -based nanofibers for specific use in wastewater to generate H_2 and clean water concurrently. Meanwhile, Cu-EDTA is a potential wastewater which can be used as sacrificial reagent for co-generation of H_2 and clean water via TiO_2 photocatalysis. Using Cu-EDTA as sacrificial reagent represents opportunities to eliminate the need for complex and chemical intensive synthesis process to improve TiO_2 's efficiency for treating Cu-EDTA, thus conserving the chemical resources and making photocatalysis a more affordable and simpler treatment option. Furthermore, it may open the door to a new synthesis route for TiO_2 -based composite nanofibers i.e. TiO_2 with CuO deposited composite nanofibers. Overall, continuous effort is necessary to identify, design and overcome the limitation of TiO_2 photocatalysts via electrospinning for use in wastewater in particular, to generate H_2 and reclaim clean water simultaneously. This would reinforce the environmental prospect and viability of photocatalytic H_2 generation over TiO_2 .

CHAPTER 3 MATERIALS AND METHODOLOGY

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3.1 Introduction

This chapter describes all the materials used and methodologies adopted in achieving the objectives of this study. Materials and synthesis methods to fabricate TiO₂ and TiO₂ composite nanofibers will be detailed out first of all, followed by the characterization methods employed to analyze and verify the nanofibers produced, and finally the experimental design, materials and setup for investigating the photocatalytic performance of the nanofibers to produce H₂ and clean water concurrently.

3.2 Materials for TiO₂ and TiO₂ composite nanofibers synthesis

Ethanol

Analytical grade, obtained from Sigma Aldrich. Ethanol was used without further purification as a solvent for TiO₂ and TiO₂ composite precursor solutions preparation.

Acetic acid

Analytical grade, obtained from Sigma Aldrich. Acetic acid was used without further purification to control hydrolysis of the TiO₂ and TiO₂ composite precursor solutions preparation.

Polyvinylpyrrolidone (PVP)

Analytical grade with a molecular weight (MW) of 1 300 000, obtained from Sigma Aldrich. PVP was used to provide viscosity to the precursor solutions, thus facilitating the electrospinning of the precursor solutions into nanofibers.

Tetra-n-butylorthotitanate (Ti(OC₄H₉)₄) or (Ti(oBu)₄)

Analytical grade, obtained from Sigma Aldrich. Ti(oBu)₄ was used as the precursor for the synthesis of TiO₂ and TiO₂/CuO composite nanofibers.

Copper 2-ethyl hexanoate (Cu[CH₃(CH₂)₃CH(C₂H₅)CO₂]₂)

Analytical grade, obtained from Sigma Aldrich. CH₃(CH₂)₃CH(C₂H₅)CO₂)₂Cu was as one of the precursors for the synthesis of TiO₂/CuO composite nanofibers.

3.3 Synthesis of bare TiO₂ and TiO₂ composite nanofibers via Electrospinning

3.3.1 Bare TiO₂ nanofibers

Ethanol and acetic acid were mixed at a ratio of 4:1 by volume to obtain a mixture of 10 mL. 680 mg of PVP was then dissolved in the 10 mL mixture, followed by

the addition of 2.3 mL $\text{Ti}(\text{oBu})_4$. The precursor solution was mixed together at room temperature using a magnetic stirrer for 6 hours to obtain a homogenous clear solution. The morphology was controlled by maintaining the humidity at $< 40\%$ using N_2 gas throughout the electrospinning process to prevent pre-mature hydrolysis of the precursor solution (Li and Xia 2003, Li, McCann et al. 2006). Subsequently, the precursor solution was loaded into a hypodermic syringe with a 1.1 mm diameter stainless steel nozzle (Li and Xia 2003). An electrical potential of approximately 1.1 kV/cm was applied between the nozzle and an aluminium foil collector. A dense nanofiber webs of PVP/ $\text{Ti}(\text{oBu})_4$ composite were consequently obtained at the collector. The self-assembled electrospinning setup is illustrated in Figure 3.1. At the end of the electrospinning process, the nanofiber webs were left in air for at least 2 hours for complete hydrolysis. Finally, the nanofibers webs were calcined in the air at 450°C for 1 hr at the temperature increase rate of $0.5^\circ\text{C}/\text{min}$ to obtain TiO_2 nanofibers.

Figure 3.1 Schematic diagram of the electrospinning setup used for nanofiber fabrication

3.3.2 TiO₂/CuO composite nanofibers

Ethanol and acetic acid were mixed at a ratio of 4:1 by volume. PVP of 7% wt was then dissolved in the mixture, followed by the addition of appropriate amount of Ti(oBu)₄ and Cu[CH₃(CH₂)₃CH(C₂H₅)CO₂]₂ to prepare a blend consisting of 1% mol Cu (1% Cu), 3% mol Cu (3% Cu), 6% mol Cu (6% Cu), 9% mol Cu (9% Cu) and 12% mol Cu (12% Cu). The electrospinning procedure and operating conditions followed that for the synthesis of TiO₂ nanofibers in Section 3.3.1. The hydrolysed nanofiber webs of PVP/Ti(oBu)₄/ Cu[CH₃(CH₂)₃CH(C₂H₅)CO₂]₂ were calcined in the air at 450°C for 45 minutes at the temperature increase rate of 0.5°C/min to obtain TiO₂/CuO composite nanofibers.

3.3.3 TiO₂/CuO composite nanofibers via wet - impregnation method

TiO₂/CuO composite nanofibers were also fabricated via the conventional wet-impregnation (WI) method according to the procedure reported in our previous study (Xu, Ng et al. 2010) for comparison with that synthesized via the innovated methods herein. Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) was diluted with deionized (DI) water at the optimum concentration (Xu, Ng et al. 2010). The electrospun bare TiO₂ nanofibers were added into the Cu(NO₃)₂ solution at a ratio of 0.2 g/10 ml. The mixture was subjected to ultrasonication for 2 hours and subsequently dried in an oven at 103 °C overnight to remove the water and finally calcined at 450 °C for 4 hours to obtain the final photocatalyst.

3.4 Characterization Methods

3.4.1 X-ray Powder Diffraction (XRD)

The crystalline structure of TiO₂ and TiO₂ composite nanofibers were obtained using a Bruker D8 Advance XRD with monochromated high-intensity Cu K α radiation (λ = 1.5418 Å), operated at 40 kV and 40 mA. The scanning rate was 2 °/min. Scherrer equation which is well-used to measure the crystal size according to the XRD pattern was adopted for the estimation of nanocrystalline size. The

Scherrer Equation is $L = K\lambda / \beta \cos \theta$ where L , K , λ , β , and θ are size of particles in nm, a constant of 0.891, wavelength of X-ray, full width at half maximum (FWHM) of the XRD peak, and angle of diffraction, respectively (Chen and Mao 2007, Ohtani 2008). The content of anatase TiO_2 relative to rutile TiO_2 phase was quantified based on the equation $X_A = 1/(1 + 1.26I_R/I_A)$, where X_A denotes content of anatase phase, and I_R and I_A are intensities of the most intense XRD peaks for anatase and rutile phases, respectively (Ohtani 2008).

3.4.2 Field Emission Scanning Electron Microscopy (FESEM)

The morphologies of TiO_2 and TiO_2/CuO composite nanofibers were investigated using FESEM, JEOL, JSM-7600F. The nanofibers were also observed via a scanning transmission electron microscopy (STEM) attached to FESEM, JEOL, JSM-7600F, working at an accelerated voltage of 30 kV. The STEM detector provides two dimensional information of the samples under a dark or bright field.

3.4.3 Transmission Electron Microscopy (TEM)

The morphologies and microstructure of TiO_2 , and TiO_2/CuO composite nanofibers were observed by TEM (JEOL JSM-1400) working at an accelerated voltage of 200 kV. The crystallization and crystal lattice of all nanofibers were observed on the high resolution transmission electron microscopy (HRTEM, JEOL JEM-2010) working at an accelerated voltage of 200 kV.

3.4.4 Energy Dispersive X-ray Spectrometer (EDS)

Elemental composition of TiO_2 and TiO_2/CuO composite nanofibers were analyzed using EDS attached to the FESEM, JEOL, JSM-7600F, working at an accelerated voltage of 20 kV.

3.4.5 Brunauer, Emmett, and Teller (BET)

The BET specific surface area were determined at liquid nitrogen temperature (77K) using a Micromeritics ASAP 2040 system. The samples were degassed at 200°C for 3 hours prior to measurement. The Barret-Joyner-Halenda (BJH) method was employed to obtain the pore size distribution of the electrospun nanofibers.

3.4.6 UV-visible Spectroscopy

The absorption spectra of the electrospun nanofibers were recorded using the Thermo Scientific Evolution 300 UV-Vis spectrometer (Thermo Fisher Scientific, Massachusetts, USA) equipped with the integrating sphere and a xenon lamp source. The spectra were further analyzed to obtain new indirect bandgap energy of the photocatalysts by the Kubelka-Munk function which converts diffusive reflectance measurements into the equivalent absorption coefficients (Ohtani 2008, Liu, Bai et al. 2011). It is the photon energy ($h\nu$) value when $[F(R_\infty)]^{0.5}=0$, obtainable when the vertical segment of the plot of $[F(R_\infty)]^{0.5}$ against $h\nu$ is extended to intersect the X-axis ($h\nu$) (Ng, Xu et al. 2010).

3.4.7 X-ray Photoelectron Spectroscopy (XPS)

The chemical composition and oxidation states of all elements incorporating the electrospun nanofibers were determined via XPS (Kratos Axis Ultra Spectrometer) with a monochromic Al K α excitation source at 1486.7 eV, with a voltage of 15 KV and an emission current of 10 mA. All binding energies were referenced to C 1s at 284.6 eV.

3.4.8 Thermal Gravimetric Analysis (TGA)

Thermal stability of nanofibers was determined using the Perkin Elmer TGA model TGA7 between 23°C to 800°C at a heating rate of 5°C/min., under atmospheric conditions.

3.4.9 Photoluminescence Analysis (PL)

Fluorolog-3 spectrofluorometer (Horiba Scientific, New Jersey, USA) was used to conduct PL analysis at an excitation wavelength of 300 nm. The purpose of PL analysis is to determine the separation tendency of the photo-generated charges.

3.5 Evaluation of Photocatalytic Performance

All photocatalytic performance test was carried out using the reactor setup as illustrated in Figure 3.2. It consists of a 270 mL inner irradiation type Pyrex reactor.

UV-visible light source was supplied by a 400W high pressure Hg lamp (Riko, UVL-400HA) while visible light source was supplied by a 360W high pressure Na lamp (Riko, HNL-360A). The distance between the light source and the suspended photocatalysts was approximately 1.0 cm. Re-circulated tap water was utilized as heat exchange cooling water to maintain a constant reactor temperature of 298K (25 °C). Volumetric method was adopted to quantify the continuous generation of H₂ throughout a reaction duration. The generated H₂ volume and pressure which would result in water displacement into a beaker was measured using a weighing scale (Figure 3.2) and logged in using a data logger for further calculation using the formula $PV = nRT$; where $P = 1 \text{ atm}$, $V = \text{volume of H}_2 \text{ (L)}$ (calculated from density = mass/volume), $n = \text{number of mol of H}_2 \text{ (mol)}$, $R = \text{gas constant (0.082 L atm K}^{-1} \text{ mol}^{-1})$, and $T = 298 \text{ K (25 °C)}$. The number of mol of H₂ could be converted to $\mu\text{mol/hr}$ as follows:

$$\text{amount of H}_2 (\mu\text{mol}) = \text{amount of H}_2 (\text{mol}) \times 10^6$$

$$\text{H}_2 \text{ evolution rate } (\mu\text{mol/hr}) = \text{amount of H}_2 (\mu\text{mol}) \div \text{duration of a reaction (hours)}$$

Furthermore, gas produced from the photocatalytic reaction was qualitatively analyzed using a TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A) (Xu and Sun 2009, Xu, Du et al. 2011).

Figure 3.2 Schematic diagram of the H₂ generation photocatalytic reactor setup

3.5.1 Photocatalytic performance of TiO₂ nanofibers

Electrospun TiO₂ nanofibers was tested for its concurrent photocatalytic H₂ and clean water generation test in 0.8 mM copper-ethylene diamine tetra acetic acid (Cu-EDTA) solution. UV-visible light was used as the source of activation. Synthetic Cu-EDTA wastewater solution was prepared by dissolving equal molar amounts of copper nitrate (Cu(NO₃)₂·3H₂O) and sodium EDTA (C₁₀H₁₄N₂Na₂O₈·2H₂O) in deionized (DI) water (18.2 MΩ.cm at 25°C). Concentration of the suspended TiO₂ nanofibers in the reacting solution was 0.5 g/L. The effect of pH on the photocatalytic reaction was investigated at pH 4, 6, and 10 where pH of the Cu-EDTA solution was adjusted using diluted sodium hydroxide (NaOH) and diluted nitric acid (HNO₃). Following a purge with N₂ gas for 30 min to de-aerate the reactor, dark and photolysis experiments were carried out for 4 hrs to obtain a baseline for organic removal and H₂ generation in the absence of light only and the absence of photocatalysts only, respectively. In all subsequent photocatalysis reaction test, the suspension was stirred in the dark for 1 hr to achieve a dark adsorption-desorption equilibrium between the organometallic substrates and the photocatalysts prior to light irradiation. An aliquot of 5 mL was sampled and immediately filtered through a Millipore filter of 0.45 μm every 10 min for water quality analysis. The filtered aliquot was measured for its total organic carbon (TOC) and Cu content using a Shimadzu TOC analyzer model TOC-V CSH and inductively coupled plasma optimal emission spectrometry (ICP OES) (Dionex ISC-1000), respectively. All experiments were carried out in triplicates to get averaged data for analysis. EDTA solution without the presence of Cu ions was tested under the same experimental conditions to compare and investigate the influence of Cu-EDTA complex in photocatalytic H₂ generation. The used TiO₂ nanofibers with Cu deposited on them (herein after termed as Cu-deposited TiO₂) were collected and washed briefly with DI water to remove excess organic oxidation by-products. Subsequently they were dried overnight at 105°C in an oven and stabilized via calcinations at 450 °C for 1 hr to yield TiO₂/CuO composite nanofibers (herein after termed as reclaimed TiO₂/CuO composite (TiO₂/CuO(A))). In order to study the future potential of this recovery and reclaim approach, TiO₂/CuO(A) were tested for its photocatalytic H₂ and clean water production

efficiency from methanol solution (10% v/v) using the same reactor setup for 3 cycles.

3.5.2 Photocatalytic performance of electrospun TiO₂/CuO composite nanofibers

The TiO₂/CuO composite nanofibers (synthesized via electrospinning the innovative precursor solutions) (TiO₂/CuO(B)) were suspended at a concentration of 0.5 g/L into sacrificial reagent comprising 1:9 v/v methanol-water mixtures. Prior to irradiation and reaction, the reactor was purged with nitrogen gas for 30 minutes to de-aerate the reactor. Subsequently, the slurry mixture was continuously mixed using a magnetic stirrer to ensure homogeneity throughout the reaction. The as-prepared bare TiO₂ nanofibers and P25 were also tested for H₂ generation for comparison. TOC was measured to investigate the organic degradation. All experiments were carried out in triplicates to get averaged data for analysis.

3.5.3 Application of TiO₂/CuO composite nanofibers in other model wastewater solutions

Both TiO₂/CuO(A) and TiO₂/CuO(B) were further investigated for their photocatalytic efficiency under both UV-visible and visible light sources in other model wastewater solutions namely glycerol (a common waste by-product from the biodiesel production industry) and Acid Orange II (AO7, a common dye pollutant). 5% (v/v) glycerol and 20 mg/L AO7 were used in this study. The concentration of photocatalysts suspended was 0.4 g/L. Prior to irradiation and reaction, the reactor was purged with nitrogen gas for 30 minutes to de-aerate the reactor. Subsequently, the slurry mixture was continuously mixed using a magnetic stirrer to ensure homogeneity throughout the reaction. TOC was measured to investigate the organic degradation efficiency. This was carried out to predict their application prospects. The amount of Cu in the reaction solution was determined after each reaction cycle using the ICP OES to study the stability of both photocatalysts. Leachability test was carried out additionally at pH 2 and pH 12 in diluted HNO₃ and diluted NaOH

respectively, to predict the operational pH spectrum for both photocatalysts. All experiments were carried out in triplicates to get averaged data for analysis.

3.5.4 Investigation of the relationship between physicochemical properties and photocatalytic efficiency

This study was taken into a deeper phase to gain an in-sight of the fundamental relationship between physicochemical properties of the innovated TiO_2/CuO composite nanofibers and its photocatalytic efficiency. Temperature was varied at 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C during calcinations of the $\text{PVP}/\text{Ti}(\text{oBu})_4/\text{Cu}[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2$ composite nanofiber webs to realize this study. TiO_2/CuO composite nanofibers which were synthesized at different calcinations temperature were characterized comprehensively and tested for their photocatalytic H_2 generation and TOC removal in sacrificial reagent comprising 1:9 v/v methanol-water mixtures using the setup in Figure 3.2. 0.5 mg/L photocatalysts were used. All experiments were carried out in triplicates to get averaged data for analysis.

CHAPTER 4 ELECTROSPUN ONE-DIMENSIONAL (1D) TiO₂ NANOFIBERS FOR PHOTOCATALYTIC H₂ AND CLEAN WATER GENERATION

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4.1 Introduction

The potential of 1D TiO₂ nanotubes over its nanoparticle counterpart for an efficient photocatalytic H₂ and Cu²⁺ removal have been demonstrated previously in our group (Xu, Ng et al. 2011). Nevertheless, the synthesis method entailed more complex procedures and use of more resources. Electrospun TiO₂ nanofibers have been demonstrated to exhibit higher H₂ generation from methanol solution than that by TiO₂ nanofibers synthesized via hydrothermal method (Chuangchote, Jitputti et al. 2009). Furthermore, the use of methanol-Cu²⁺ and methanol aqueous solution did not seem realistic and viable in a long run. Moving forward, in order to adopt a simple synthesis method of photocatalysts without compromising its photocatalytic efficiency, a feasibility study of using electrospun TiO₂ nanofibers for photocatalytic treatment of a wastewater was initiated in this chapter. As discussed earlier, electrospinning was chosen as it is a facile synthesis method compared to the conventionally used hydrothermal method (Chuangchote, Jitputti et al. 2009). Cu-EDTA was employed to eliminate the need of methanol addition and as a novel 'sacrificial reagent' in the form of waste water from the industry for clean energy fuel and clean water co-generation. The synergy of 1D TiO₂ nanofibers and Cu-EDTA was also employed to facilitate the test of another interesting hypothesis for the first time; the feasibility of direct reclamation of the used TiO₂ photocatalyst with Cu deposited on it. This chapter presents all results and discussion comprising 1) characterization of electrospun TiO₂ nanofibers, 2) photocatalytic H₂

and clean water generation, 3) reclamation and characterization of used TiO_2 nanofibers, 4) Application prospect of the reclaimed photocatalysts, and 5) overall mechanism of this synergistic reaction.

4.2 Characterization of Electrospun TiO_2 Nanofibers

Figures 4.1 shows the morphology of the calcined bare TiO_2 nanofibers observed by the FESEM. The average diameter was about 100 nm. With a length of more than 10 μm even after calcinations, the nanofibers exhibited high aspect ratio of around 30-50. The highly consistent morphology without the presence of any bead has witnessed the positive effect from the humidity control using the N_2 gas purging which has resulted in a sufficient control of the surface tension of the precursor solution (Li and Xia 2004). The loss of PVP during calcinations has resulted in a very rough and porous surface structure of the nanofibers (Fig. 4.1(b)). The porous structure would render the photocatalysts with high specific surface area thus reaction sites for adsorption and photocatalytic reaction of Cu-EDTA (Pan, Dou et al. 2010).

Figure 4.1 (a) Low magnification FESEM image of TiO_2 nanofibers, (b) High magnification FESEM image of TiO_2 nanofibers showing detailed porous surface morphology

XRD pattern as shown in Fig. 4.2 clearly indicates that the as-synthesized TiO_2 nanofibers were well-crystallized into anatase TiO_2 phase (JCPDS file No. 21-1272) (Ng, Xu et al. 2010).

Figure 4.2 XRD pattern of the TiO₂ nanofibers

A surface analysis using the N₂ adsorption-desorption isotherm technique showed that TiO₂ nanofibers were mesoporous as characterized by the type IV isotherm curve with obvious H3-type hysteresis (Fig. 4.3). The BJH analysis further affirmed the mesoporosity nature of TiO₂ nanofibers since they showed a narrow pore size distribution of between 2-20 nm (Fig. 4.4) (Sing 1995). A mesoporous structure is desirable to enhance the photocatalytic reaction as it enables fast diffusion of reactants through the photocatalysts thus facilitating access to the reactive sites (Pan, Sun et al. 2010). The BET specific surface area of the TiO₂ nanofibers was 34.30 m²/g, which is comparable to that of the commercial TiO₂ P25 (34.40 m²/g).

Figure 4.3 N₂ adsorption/desorption isotherm curve of the TiO₂ nanofibers

Figure 4.4 BJH pore size distribution of the TiO₂ nanofibers

As such, the as-synthesized TiO₂ nanofibers may represent a promising candidate for efficient photocatalytic treatment of Cu-EDTA to generate H₂ and clean water ascribing to the synergy between (1) its 1D long nanofibrous structure (Fig. 4.1) which would have low aggregation tendency thus ensuring optimum specific surface area for pollutants adsorption, facilitating recovery and reusability of the used photocatalysts (Pan, Dou et al. 2010) as well as enhancing charges separation

for oxidation and reduction processes (Choi, Kim et al. 2010), (2) its well-crystallized anatase TiO_2 phase which minimizes charges recombination and ensures good interparticle charge transfer, and (3) its mesoporous structure which would promote diffusivity of reactants through the photocatalysts hence high reactants mass transfer (Pan, Sun et al. 2010).

4.3 Photocatalytic Organic and Cu^{2+} Removal with Co-generation of H_2 and Clean Water

The as-synthesized TiO_2 nanofibers were tested to co-generate H_2 and clean water through photocatalytic treatment of an organometallic wastewater pollutant model, Cu-EDTA, under UV-visible irradiation. Its efficiency is compared against that of a pure EDTA solution without the presence of Cu^{2+} ions. Total organic carbon (TOC) and Cu^{2+} removal were indirect monitoring parameters for the degradation of Cu-EDTA thus the clean water generation. In the case of EDTA, only TOC was monitored. As shown in Figure 4.5 (a), at the end of the 4-hrs irradiation, nearly 2 times more H_2 generation rate of approximately $251 \mu\text{mol/hr}$ was obtained from Cu-EDTA than that from EDTA over TiO_2 nanofibers. TOC removal from Cu-EDTA was observed to be nearly 1.5 times higher than that from EDTA. No appreciable H_2 generation and TOC removal was observed both in the dark and during photolysis (in the absence of photocatalysts) signifying the essential role of TiO_2 nanofibers for photocatalytic treatment of both Cu-EDTA and EDTA. Figure 4.5(b) shows the continuous percentage removal of TOC and Cu^{2+} from Cu-EDTA over the TiO_2 nanofibers throughout the 4-hrs reaction. The more superior H_2 generation rate and TOC removal in Cu-EDTA than EDTA have signified the dominant role of Cu from Cu-EDTA in promoting the photocatalytic reaction over TiO_2 .

Figure 4.5 (a) Photocatalytic TOC removal (%) and H₂ generation rate for Cu-EDTA and EDTA, and (b) Photocatalytic removal of TOC (%), Cu (%), and H₂ generation over 4 hr reaction in Cu-EDTA

Table 4.1 depicts the effect of pH on the photocatalytic reaction. Shortest time was required at pH 4 for 90% of the Cu²⁺ to be removed from the solution. Protonated TiO₂ surface under acidic condition facilitated the adsorption of the anionic Cu-EDTA (Chung and Rho 1999, Yang and Davis 2000), thus promoting the photocatalytic oxidation (PCO) of the adsorbed Cu-EDTA by the photogenerated holes, and subsequently the decomplexation and photocatalytic reduction (PCR) of

Cu^{2+} on TiO_2 by the photogenerated electrons. Meanwhile, possible protonation of Cu-EDTA could happen at low pH, leading to decomplexation in the bulk solution prior to adsorption on TiO_2 (Yang and Davis 1999). TOC removal was nevertheless less favourable at pH 4 than that at pH 6 and 10. At higher pH, despite the presence of OH^- which would pose a competition with Cu-EDTA for adsorption and reaction sites on TiO_2 (Chung and Rho 1999), its formation as OH radical ($\text{OH}\cdot$) by the photogenerated holes (Kim, Lee et al. 2003) would eventually facilitate Cu-EDTA oxidation in the bulk solution. The higher TOC removal at higher pH further suggested that the overall TOC reduction could be enhanced by OH^- , in addition to the adsorption and oxidation by the holes. In the case where PCO of Cu-EDTA took place in the bulk solution, the PCR of Cu^{2+} could be delayed due to the additional path required for the decomplexed Cu^{2+} to reach and adsorb onto TiO_2 , as evidenced by the longer Cu^{2+} removal at pH 6 and 10. However, negatively charged TiO_2 under basic condition might counter this effect by favouring the adsorption of Cu^{2+} (Chung and Rho 1999, Yang and Davis 2000). Overall, regardless of solution pH, approximately 50% TOC and 90% of Cu^{2+} removal was eventually achieved within 1 hr of reaction. Meanwhile, the combined effect of H^+ as the precursor to H_2 production (Choi 2007, Xu and Sun 2009) as well as PCR of Cu^{2+} as reduction sites on TiO_2 (Xu, Ng et al. 2011) seemed to have promoted H_2 generation at pH 4; despite the small differences on H_2 evolution rate between all pH values. This part of work showed that H_2 and clean water can be generated concurrently from Cu-EDTA using electrospun TiO_2 nanofibers.

Table 4.1 Effect of solution pH on photocatalytic reaction

pH condition (Cu-EDTA)	Time to achieve 90% Cu reduction (min)	TOC removal after 4 hours reaction (%)	H_2 evolution ($\mu\text{mol/hr/g}$)
pH 4	10	57.5	2293.0
pH 6	40	71.0	1930.3
pH 10	50	70.0	2196.6

4.4 Reclamation of Used TiO_2 (Cu-deposited TiO_2) into TiO_2/CuO Composite Nanofibers ($\text{TiO}_2/\text{CuO(A)}$) and Characterization

Upon heat treatment at 450 °C for 1 hr, the used TiO_2 nanofibers (Cu-deposited TiO_2) were reclaimed into TiO_2/CuO composite nanofibers ($\text{TiO}_2/\text{CuO(A)}$). An in-depth characterizations of $\text{TiO}_2/\text{CuO(A)}$ were carried out and compared with that of TiO_2 nanofibers to verify the formation of $\text{TiO}_2/\text{CuO(A)}$. Figure 4.6 shows the sustained length and diameter in $\text{TiO}_2/\text{CuO(A)}$ which would be advantageous for the subsequent application and recovery because these properties are important to facilitate inter-particle charges transfer and to prevent agglomeration of the nanofibers (Pan, Sun et al. 2010).

Figure 4.6 Low magnification FESEM image of $\text{TiO}_2/\text{CuO(A)}$

$\text{TiO}_2/\text{CuO(A)}$ has remained a mesoporous property like TiO_2 nanofibers after the reaction, as characterized by the type IV isotherm curve with obvious H3-type hysteresis (Fig. 4.7) (Sing 1995). The mesoporous nature of $\text{TiO}_2/\text{CuO(A)}$ was further corroborated by the BJH analysis where a narrow pore size distribution of

between 2-20 nm was observed (inset of Fig. 4.7) (Sing 1995). Figure 4.8 shows a high-magnification STEM-FESEM image of a single strain of $\text{TiO}_2/\text{CuO(A)}$. Figure 4.8 (a)-(b) depict the possible aggregation of Cu which was however generally rare as seen in Fig. 4.6, while Fig. 4.8(c) confirms the presence of both Ti and Cu on $\text{TiO}_2/\text{CuO(A)}$. Elemental analysis showed a composition of 22.7%mol Cu. The mapping images as shown in Figs. 4.8(d)-(f) further supported the co-existence of well-dispersed Ti, Cu, and O elements, possibly facilitated by the mesoporosity (Fig. 4.7) and the ultralong 1D structure of the nanofibers (Figs. 4.6). A good Cu dispersion is highly desirable to attain an optimized elemental contact between TiO_2 and CuO heterojunctions which thus would enhance the transfer and separation of the photogenerated charges for a more efficient photocatalytic reaction (Bokhimi, Morales et al. 1997, Yoong, Chong et al. 2009).

Figure 4.7 N_2 adsorption/desorption isotherm curve of TiO_2 nanofibers (black) and $\text{TiO}_2/\text{CuO(A)}$ (red), and BJH pore size distribution (inset) of TiO_2 nanofibers (black) and $\text{TiO}_2/\text{CuO(A)}$ (red)

Figure 4.8 (a) High magnification dark field FESEM-STEM image of a single $\text{TiO}_2/\text{CuO(A)}$, (b)-(c) EDX spectrums for the indicated points on the nanofiber in (a), Elemental mapping for the selected area in (a) for (d) Ti element, (e) Cu element, and (f) O element

The reduced BET specific surface area in $\text{TiO}_2/\text{CuO(A)}$ compared to TiO_2 nanofibers as shown in Table 4.2 is consistent with the observation in Figs. 4.8, further affirming the deposition of Cu elements on and within TiO_2 nanofibers. Meanwhile, the increased BET specific surface area of $\text{TiO}_2/\text{CuO(A)}$ compared to Cu-deposited TiO_2 has suggested that the organics have been removed during calcinations.

Table 4.2 Summary of BET specific surface area of the photocatalysts

Materials	BET specific surface area (m^2/g)
(a) TiO_2 nanofibers	34.30
(b) Cu-deposited TiO_2	2.00
(c) $\text{TiO}_2/\text{CuO(A)}$ (from calcination of (b))	14.25
(d) Regenerated $\text{TiO}_2/\text{CuO(A)}$	13.11

The HRTEM image as depicted in Figure 4.9 further elucidates the closely contacted TiO_2 -CuO heterojunctions. Both the (101) plane of anatase TiO_2 and the (111) plane of CuO were well-evidenced by the lattice fringes of 0.325 nm and 0.253 nm, respectively (Mor, Varghese et al. 2008, Ng, Xu et al. 2010, Gouma and Lee 2011).

Figure 4.9 High magnification HRTEM image showing the corresponding crystal lattice of anatase TiO_2 and CuO with an inset showing the full range XRD patterns for TiO_2 nanofibers and $\text{TiO}_2/\text{CuO(A)}$

The XRD pattern in Figure 4.10(a) revealed that in addition to anatase TiO_2 (JCPDS file No. 21-1272) (Ng, Xu et al. 2010), CuO was present. A close-up XRD pattern plotted across the region of $2\theta = 30^\circ - 45^\circ$ was given in Fig. 4.10(b) to provide a clear view where the peaks observed at $2\theta = 36.5^\circ$ and $2\theta = 38.8^\circ$ could be ascribed to the (111) plane and (002) plane of CuO, respectively (Mor, Varghese et al. 2008), in consistent with the observed HRTEM image (Fig. 4.9).

Figure 4.10 (a) Full range XRD patterns for TiO₂ nanofibers and TiO₂/CuO(A), (b) Close-up XRD patterns for TiO₂ nanofibers and TiO₂/CuO(A) from $2\theta = 30^\circ - 45^\circ$.

The absorbance spectra of TiO₂ and TiO₂/CuO(A) in the UV-Vis light region of between 350-800 nm were illustrated in Fig. 4.11. The absorption edge in the UV light region has been red-shifted for TiO₂/CuO(A), suggesting the successful incorporation of the CuO into TiO₂ nanofibers as well-witnessed in the HRTEM image (Fig. 4.9) and XRD patterns (Fig. 4.10). In addition, the photoresponse in the

visible light region was significantly intensified likely due to the presence of CuO which has a small bandgap of 1.2 eV thus capable of absorbing both the UV and visible regions of the solar spectrum (Yu, Yu et al. 2007). The enhanced sensitivity and absorption in the visible light region could enhance the photogeneration of electrons and holes for photocatalytic reaction.

Figure 4.11 The UV-visible spectra of TiO_2 nanofibers and $\text{TiO}_2/\text{CuO(A)}$

The addition of CuO has resulted in a lower PL spectra by $\text{TiO}_2/\text{CuO(A)}$ than that by TiO_2 nanofibers (Fig. 4.12). A lower PL spectra intensity implies a lower recombination tendency of the photogenerated charges (Ng, Xu et al. 2010). The energy potential differences which existed between the conduction band (CB) of TiO_2 and that of the CuO have promoted the migration of the photogenerated electrons from the CB of TiO_2 to that of CuO. This has further corroborated the advantage of good elemental dispersion and close proximity between TiO_2 and CuO heterojunctions as shown in Figs. 4.8 and Fig. 4.9; which implied that the separation and hence the life span and utilization of photogenerated charges could be enhanced for photocatalytic reaction.

Figure 4.12 Photoluminescence spectra of TiO₂ nanofibers and TiO₂/CuO(A)

The chemical composition and elemental states of TiO₂/CuO(A) were analyzed using the XPS analysis (Fig. 4.13). The binding energy for C1s peak at 284.6 eV was used as the reference for calibration. The survey spectrum (Fig. 4.13(a)) witnesses the existence of Ti, Cu, and O in the regenerated TiO₂ nanofibers. The high resolution spectrums for Ti, O, and Cu were given in Fig. 4.13(b)-(d). The characteristic peaks for Ti⁴⁺ at the binding energy of 458.0 eV and 464.0 eV which were indicative of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. The peaks at binding energy of 529.5 eV which was evidence of O 1s in TiO₂ and CuO (Xu, Du et al. 2011) whereas peaks at higher binding energy implied contamination by atmospheric hydroxides onto the surface of the composite nanofibers (Xu, Du et al. 2011). The valence state of Cu was +2, as corroborated by the peaks around the binding energy of 933.9 eV and 953.9 eV ascribing to the Cu 2p_{3/2} and Cu 2p_{1/2} of Cu²⁺ in CuO (Wu and Lee 2004), respectively. The existence of Cu²⁺ from CuO in the composite nanofibers was further confirmed by the characteristic shakeup satellite peaks around 942.0 eV and 962.0 eV (Li, Dimitrijevic et al. 2008).

Figure 4.13 (a) XPS survey spectrum for $\text{TiO}_2/\text{CuO(A)}$; High resolution XPS spectrum of $\text{TiO}_2/\text{CuO(A)}$ for (b) Ti 2p, (c) Cu 2p, and (d) O 1s

On the basis of the characterizations and analysis, it is reasonable to state that Cu has been successfully loaded into the TiO_2 nanofibers and after calcinations, formed $\text{TiO}_2\text{-CuO}$ composite ($\text{TiO}_2/\text{CuO(A)}$). $\text{TiO}_2/\text{CuO(A)}$ could be a potential nanomaterial candidate for photocatalytic reaction. Unlike the conventionally adopted method such as wet-impregnation, hydrothermal and sol-gel which entail use of additional chemical or complex synthesis steps to incorporate Cu on the surface of the TiO_2 photocatalysts (Kim and Ihm 2007, Xu and Sun 2009, Yoong, Chong et al. 2009, Xu, Du et al. 2011), the comprehensive characterization study herein has revealed that the recovered Cu from Cu-EDTA wastewater can be utilized directly as the precursor to synthesize $\text{TiO}_2\text{-CuO}$ composite almost instantly in a more sustainable manner by tapping into the benefits of 1D TiO_2 nanofibers. With this, not only the non-renewable chemical resource could be conserved, there was also opportunity for attaining zero waste discharge from the wastewater treatment, assuming that a proper drain segregation has been implemented upstream

at the point of wastewater generation to prevent mixing of variety of waste components.

4.5 Photocatalytic Efficiency of $\text{TiO}_2/\text{CuO(A)}$

The $\text{TiO}_2/\text{CuO(A)}$ were tested for their photocatalytic function to generate H_2 from 10% v/v methanol. At the end of 4 hr reaction, $\text{TiO}_2/\text{CuO(A)}$ exhibited the highest H_2 generation of approximately 6900 μmol under UV-visible light, as shown in Fig. 4.14. Both P25 and as-synthesized TiO_2 nanofibers demonstrated negligibly low photocatalytic H_2 generation compared to $\text{TiO}_2/\text{CuO(A)}$.

Figure 4.14 Photocatalytic H_2 generation over 4 hr reaction in 10% v/v methanol by P25, as-synthesized TiO_2 nanofibers, $\text{TiO}_2/\text{CuO-WI}$, and $\text{TiO}_2/\text{CuO(A)}$

$\text{TiO}_2/\text{CuO(A)}$ exhibited higher photocatalytic H_2 generation capacity compared to $\text{TiO}_2/\text{CuO-WI}$ which were prepared via the conventional wet-impregnation method; implying the feasibility and potential of integrating Cu-EDTA and 1D TiO_2 nanofibers to synthesize TiO_2/CuO composite in a more green and friendly manner as it is straight forward without complex steps and additional chemicals while not compromising on the overall photocatalytic efficiency when compared with $\text{TiO}_2/\text{CuO-WI}$. The synergy between all the enhanced physicochemical properties of $\text{TiO}_2/\text{CuO(A)}$ could have facilitated a good dispersion and contact between TiO_2

and CuO heterojunctions and driven the net photocatalytic reaction (Lee, Bai et al. 2013). CuO in TiO₂/CuO(A) offered similar role as the Cu⁰ in TiO₂/CuO before calcinations, thus enhancing photocatalytic H₂ production (Xu, Ng et al. 2011, Lee, Bai et al. 2013). The specific surface area could be easily recovered via facile calcinations at 450 °C overnight (Table 4.2).

4.6 Mechanism Explanation

Based on the experimental data and characterization studies, the mechanism of producing clean water, H₂, and TiO₂/CuO(A) simultaneously via the photocatalytic treatment of Cu-EDTA was postulated and illustrated in Fig. 4.15.

Figure 4.15 Mechanism behind the cogeneration of H_2 , clean water and $\text{TiO}_2/\text{CuO(A)}$ from the photocatalytic treatment of Cu-EDTA using 1D TiO_2 nanofibers

The mechanism comprised the reaction that takes place in the bulk solution and on the photocatalysts. Upon harvesting of the photon energy from the simulated solar irradiation, electrons and holes responsible for the photocatalytic reaction were generated in the CB and valence band (VB) of the TiO_2 nanofibers, respectively. The photogenerated holes would react with the hydroxyl groups in the aqueous phase or on the surface of the photocatalysts, thus yielding the reactive oxidation

species (ROS) which possess strong oxidation ability. The PCO of Cu-EDTA was initiated either by the ROS in the bulk solution, or by the photogenerated holes and/or the ROS on the surface of the TiO₂ nanofibers where Cu-EDTA was adsorbed onto. Subsequently, decomplexation of the Cu²⁺ from Cu-EDTA complexes would take place, followed by the adsorption of Cu²⁺ onto TiO₂ nanofibers. (Yang and Davis 2000, Cho, Shin et al. 2006) Cu²⁺ ions in the bulk solution however would need to travel in order to access the photocatalysts prior to adsorption, and this would be more significant under high pH condition where adsorption of Cu-EDTA was challenged. Thereafter, Cu²⁺ could be reduced into Cu metal (Cu⁰) by the photogenerated electrons. (Yang and Davis 2000, Xu, Ng et al. 2011) A uniform dispersion and adsorption of Cu²⁺ was facilitated by the mesoporosity and long nanofibrous structure of the TiO₂ nanofibers (Yang and Davis 2000, Yang and Davis 2001). H₂ could be harvested by extending PCO of the remaining intermediate oxidation by-products and PCR of H₂O or H⁺. The reaction products and intermediates from the PCO of Cu-EDTA over TiO₂ photocatalysts has been well-studied and can be found elsewhere; thus is not included in this research (Yang and Davis 2000, Yang and Davis 2000, Yang and Davis 2001, Yang, Lee et al. 2006). Owing to the energy level difference between the valence of TiO₂ and Cu⁰ (Fig. 4.15), the migration of photogenerated electrons was promoted from the CB of TiO₂ to Cu⁰, thus enhancing separation of photogenerated charges on TiO₂ (Helaïli, Bessekhoud et al. 2009). These electrons would be rapidly and efficiently used up for H₂O reduction into H₂ since the redox potential of Cu⁰ is more electronegative than H₂O reduction potential (Xu, Ng et al. 2011). Under acidic condition, additional H⁺ would also enhance the H₂ generation (Table 4.1). On the surface of the TiO₂ nanofibers, Cu⁰ rendered several advantages as follows: (1) it served as an efficient reduction co-catalyst for H₂ production, (2) it promoted the separation of photogenerated charges thus a longer lifetime of the charge carriers, and (3) it extended the light sensitivity and absorption thus the charges photogeneration ability of TiO₂ nanofibers (Xu, Ng et al. 2011). Hence, H₂ generation rate from Cu-EDTA was more efficient than that from EDTA (Fig. 4.1(a)) (Ashokkumar 1998). While the Cu⁰ could also be possibly oxidized by the holes into Cu²⁺ (Xu, Ng et al. 2011), and while the PCR of the Cu²⁺ into Cu⁰ would

result in the competition for electrons to generate H_2 (Xu, Ng et al. 2011), the overall net effect of Cu^0/Cu^{2+} and Cu^{2+}/Cu^0 redox reactions were seen to be insignificant and would become negligible at one stage, especially as the reaction progressed beyond 1 hr after which almost 90% of Cu^{2+} were removed along with a continuous H_2 evolution (Fig. 4.1(b)).

4.7 Summary

Briefly, this study has showed that clean water, clean energy fuel, and $TiO_2/CuO(A)$ could be co-generated from photocatalytic treatment of Cu-EDTA through the excellent synergy rendered by extending PCO and PCR of Cu-EDTA coupled with TiO_2 nanofibers of superior physicochemical properties. With the elimination of (1) prior complex synthesis process to modify and enhance TiO_2 , (2) sacrificial reagent to enhance reaction efficiency for clean water and clean energy production, and (3) additional chemical to recover Cu, this approach has significantly enhanced the sustainability of H_2 and clean water generation via TiO_2 photocatalysis. What is more, this ingenious synergistic integration represents an adoptable alternative sustainable option to synthesize other efficient and functional composite nanomaterials from other organometallic wastewater streams, broadening its environmental application prospect.

CHAPTER 5 TiO₂ COMPOSITE NANOFIBERS VIA ELECTROSPINNING INNOVATIVE PRECURSOR SOLUTIONS FOR PHOTOCATALYTIC H₂ AND CLEAN WATER GENERATION

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5.1 Introduction

Chapter 4 has presented an advancement in our research domain through the usage of 1D TiO₂ nanofibers synthesized via electrospinning for concurrent H₂ and clean water generation from Cu-EDTA waste water, hence a simpler and more environmental friendly approach (herein after termed as 'Approach A'). In light of that, the easily reclaimed TiO₂/CuO composite nanofibers (TiO₂/CuO(A)) have demonstrated good photocatalytic potential, further extending the environmental advantage of Approach A. Nevertheless, challenge remains where aggregation of Cu on TiO₂ nanofibers was not easily controllable. Approach A is thus limited to low range of Cu-EDTA concentration as aggregation of Cu element may pose higher recombination rate of the photogenerated charges thus reducing photocatalytic efficiency of TiO₂ nanofibers and subsequently that of TiO₂/CuO(A) (Choi, Kim et al. 2010). The greatly reduced specific surface area of TiO₂ nanofibers due to the photo-deposition of the Cu element would further compound the negative effect on the photocatalytic reaction by minimizing the available active reaction sites for reactant adsorption. In order to overcome the challenge posed by aggregation while tapping the benefits of TiO₂ and CuO composite system, synthesis of TiO₂/CuO composite nanofibers was attempted by employing electrospinning of an innovated precursor solution for the first time, maintaining simplicity and synergy between TiO₂ and CuO without compromising the

physicochemical properties of the composite. The characterization and photocatalytic efficiency of the innovated TiO_2/CuO composite were comprehensively discussed in this chapter. Comparison of its photocatalytic efficiency with that of the commercial P25, as-synthesized TiO_2 nanofibers and $\text{TiO}_2/\text{CuO(A)}$ (from Approach A) was also undertaken.

5.2 Characterization of Electrospun TiO_2/CuO Composite Nanofibers

The morphology of the electrospun innovative TiO_2/CuO nanofibers (herein after termed as $\text{TiO}_2/\text{CuO(B)}$) measured by FESEM is shown in Figs. 5.1(a)-(d). The uncalcined fibrous structure of an as-spun individual composite nanofiber is illustrated in Fig. 5.1(a). Clearly, before calcinations, the surface appeared smooth, without any obvious pores. As shown in Fig. 5.1(b), after calcinations at high temperature, the length of the nanofibers remained more than 10 μm long with a typical aspect ratio of around 30-50 and beads-less. The composite nanofibers were shown to be very consistent in diameter, approximated to be less than 100 nm (Fig. 5.1(c)). Again, this high uniformity and elimination of beads suggest that the viscoelastic force and electrostatic repulsion between charges in the precursor solution were sufficiently maintained through humidity control to suppress the influence of surface tension which drives the formation of beads (Li and Xia 2004). The diameter of the calcined nanofibers decreased and the surface was rough and porous (Fig. 5.1(d)) due to the loss of PVP and other organic substances used in the preparation of the precursor solution and crystallization of anatase TiO_2 during calcinations (Li and Xia 2003). The pores were measured to be approximately between 5 – 10 nm.

Figure 5.1 FESEM images of (a) uncalcined composite nanofiber; (b)-(c) calcined $\text{TiO}_2/\text{CuO(B)}$; and (d) High magnification of calcined $\text{TiO}_2/\text{CuO(B)}$ showing detailed porous surface topography

Figure 5.2(a)-(b) shows the FESEM-STEM images of $\text{TiO}_2/\text{CuO(B)}$. The nanofibers were further affirmed to be very consistent and uniform. White spots in Fig. 5.2(a) observable on the composite nanofibers were attributed to the presence of pores on and within the composite nanofibers. Using the dark field mode of the STEM, heavy element should appear bright while lighter element should appear dark. Fig 5.2(b) illustrates the dark field mode of an individual $\text{TiO}_2/\text{CuO(B)}$ nanofiber. Due to the low voltage used (30 kV) in the FESEM system, HRTEM at 200 kV (Jeol JSM-2010) was employed to further the microstructure observation of the composite nanofibers. Fig. 5.2(c) depicts that the composite nanofibers were made up of well-grown granular nanocrystals. The SAED as shown in Fig. 5.2(d) suggested that the $\text{TiO}_2/\text{CuO(B)}$ were made up of polycrystalline structure of TiO_2 .

Figure 5.2 (a) FESEM-STEM image of $\text{TiO}_2/\text{CuO(B)}$, (b) FESEM-STEM image of $\text{TiO}_2/\text{CuO(B)}$ nanofibers under dark field mode, (c) TEM image of $\text{TiO}_2/\text{CuO(B)}$; and (d) SAED pattern of $\text{TiO}_2/\text{CuO(B)}$

HRTEM images in Figure 5.3 elucidate two distinctive lattice fringes of 0.325 nm and 0.253 nm which correspond well to the (101) plane of anatase TiO_2 (Ng, Xu et al. 2010) and the (111) plane of CuO , respectively (Cao, Hu et al. 2003, Gouma and Lee 2011).

Figure 5.3 (a) Bright field TEM image of $\text{TiO}_2/\text{CuO(B)}$ -6 (b) High magnification HRTEM image showing the corresponding crystal lattice of anatase TiO_2 and CuO from the delineated area in (a)

In the EDX spectrum observed from Fig. 5.4(a), peaks of Ti and Cu were prominent. The mapping as shown in Figs. 5.4(b)-(e) depict that Ti, Cu, and O were well-dispersed throughout the bulk of the nanocomposite materials, proving that a good interdispersion was achieved from the mixing of the precursor solution with mere magnetic stirrer. Uniform dispersion of CuO is advantageous by ensuring strong interaction between TiO_2 and CuO for migration of electrons between conduction bands thereby enhancing its charge transfer and separation for photocatalytic reaction (Bokhimi, Morales et al. 1997, Yoong, Chong et al. 2009).

Figure 5.4 (a) EDX spectrum of $\text{TiO}_2/\text{CuO(B)}$ -6, Elemental mapping of the selected area (as in Figure 5.4(b)) for (c) O element, (d) Ti element, and (e) Cu element

The surface structure of the prepared $\text{TiO}_2/\text{CuO(B)}$ was analyzed by N_2 sorption-desorption isotherm technique. The curve (Fig. 5.5(a)) revealed type IV isotherm with obvious H3-type hysteresis behavior according to IUPAC classification, which characterized the composite nanofibers to be mainly mesoporous (Sing 1995). The BJH method was employed to analyze the corresponding pore size distribution and has depicted a narrow distribution between 2-20 nm with peaking position at 6 nm (Fig. 5.5(b)). This is in close agreement with that approximated from the FESEM image in Fig. 5.1. $\text{TiO}_2/\text{CuO(B)}$ exhibited more larger pores and higher mesoporosity compared to TiO_2 and $\text{TiO}_2/\text{CuO(A)}$.

Figure 5.5 (a) N₂ adsorption/desorption isotherm curve, and (b) BJH pore size distribution of TiO₂ (black), TiO₂/CuO(A) (red) and TiO₂/CuO(B)-6 (blue)

The BET specific surface area of TiO₂/CuO(B) was in general higher than that of TiO₂ nanofibers, TiO₂/CuO(A), and even P25 (Table 5.1). This is in consistent with the higher mesoporosity and greater pore size distribution of TiO₂/CuO(B) as illustrated in Fig. 5.5. The increased specific surface area will definitely benefits the heterogeneous photocatalysis by facilitating surface adsorption of reactants and interfacial charge transfer.

Table 5.1Summary of physical properties of TiO₂ nanofibers and TiO₂/CuO(B)

Materials	BET specific surface area (m ² /g)
P25	34.40
TiO ₂ nanofibers	34.30
TiO ₂ /CuO(A)	14.25
TiO ₂ /CuO(B)-1	54.96
TiO ₂ /CuO(B)-3	56.38
TiO ₂ /CuO(B)-6	156.22
TiO ₂ /CuO(B)-9	108.14
TiO ₂ /CuO(B)-12	115.46

The XRD was used to examine the crystal phases of TiO₂/CuO(B), with TiO₂/CuO(B)-1 denotes composite with 1% mol Cu, TiO₂/CuO(B)-3 denotes composite with 3%mol Cu, and so on. As shown in Fig 5.6(a), TiO₂/CuO(B) nanofibers were indexed to anatase TiO₂ phase (JCPDS file No. 21-1272) at all Cu content used in this experiment. CuO peak was not discernable at all due to the detection limit of the XRD (Sayilkan 2007), relatively low Cu content, and the high dispersion of the Cu species within the bulk of the photocatalysts, which was in agreement with the elemental mapping in Fig. 5.4 (Sayilkan 2007, Xu, Du et al. 2011). High dispersion of Cu resulted in low aggregation of Cu species thus yielding a dimension which was below the detection of XRD (Xu, Ng et al. 2011). The close-up XRD pattern in the region of $2\theta=22^{\circ}$ - 30° (Fig.5.6(b)) clearly indicates the shift to a higher angle for all composite composition compared to that of the TiO₂ nanofibers, ascribing to the defect in the anatase TiO₂ crystal lattice due to the incorporation of Cu (Yu and Ran 2011).

Figure 5.6 (a) XRD patterns of $\text{TiO}_2/\text{CuO(B)}-1$, $\text{TiO}_2/\text{CuO(B)}-3$, $\text{TiO}_2/\text{CuO(B)}-6$, $\text{TiO}_2/\text{CuO(B)}-9$, and $\text{TiO}_2/\text{CuO(B)}-12$ nanofibers calcined at 450°C for 45 min and (b) Close-up XRD patterns for TiO_2 nanofibers, $\text{TiO}_2/\text{CuO(B)}-1$, $\text{TiO}_2/\text{CuO(B)}-3$, $\text{TiO}_2/\text{CuO(B)}-6$, $\text{TiO}_2/\text{CuO(B)}-9$, and $\text{TiO}_2/\text{CuO(B)}-12$ nanofibers calcined at 450°C for 45 min ($2\theta=22^\circ-30^\circ$)

Approximation of the crystalline size using the Scherrer equation in Table 5.2 showed a reducing trend in the crystalline size of anatase TiO_2 from approximately 18 nm to 16 nm when Cu content increases, thus further corroborating that the

addition of Cu has resulted in some degree of defects in the crystallization of the anatase TiO₂ (López-Ayala and Rincón 2011). This could corroborate the increased BET specific surface area (Table 5.1) since smaller crystal would render larger area. Meanwhile, smaller crystal size is expected to benefit the photocatalytic reaction by increasing the availability of the photogenerated electrons and holes at the surface reaction sites due to a shorter migration distance (Kudo and Miseki 2009).

Table 5.2 Summary of anatase crystal size of calcined TiO₂ nanofibers and TiO₂/CuO(B)

Materials	FHWM (degree)	Size of anatase crystal ^a (nm)
TiO ₂ nanofibers	0.443	18.2
TiO ₂ /CuO(B)-1	0.429	18.8
TiO ₂ /CuO(B)-3	0.463	17.4
TiO ₂ /CuO(B)-6	0.493	16.4
TiO ₂ /CuO(B)-9	0.497	16.2
TiO ₂ /CuO(B)-12	0.489	16.5

^a Calculated by the Scherrer equation (Chen and Mao 2007, Ohtani 2008).

TiO₂/CuO(B) had demonstrated significantly increased absorption edge in the UV region and visible light region, between 350-800 nm (Fig. 5.7(a)). A narrower bandgap of below 3.00 eV was recorded using Kubelka-Munk equation (Fig. 5.7(b)). The smaller bandgap could be formed due to the transition from the valence band of CuO to the conduction band of TiO₂, which are both in good contact as witnessed by the elemental mapping in Fig. 5.4 (Bokhimi, Morales et al. 1997). The loading of Cu into TiO₂ has changed the electronic property of the TiO₂ thus increasing the absorbance in the UV region of around 350 nm. The absorbance in the visible light region between 600-800 nm could be attributed to the smaller bandgap of CuO which were present in the composite nanofibers. In addition, coupled with the enhanced mesoporosity and large specific surface area, TiO₂/CuO(B) is expected to possess more efficient light utilization since more light scattering and reflections on the surface and within the nanostructures will take place (Liu, Bai et al. 2011).

Figure 5.7 (a) The UV-visible spectra of $\text{TiO}_2/\text{CuO(B)}$, and (b) the corresponding Kubelka-Munk transformed reflectance spectra to determine indirect new bandgap value for $\text{TiO}_2/\text{CuO(B)}$

All $\text{TiO}_2/\text{CuO(B)}$ composition showed distinctive PL signals following excitation at 300 nm. As shown in Fig. 5.8, there are three main emission peaks at approximately 400 nm, 435 nm, and 465 nm which corresponded to the band gap energy of 3.10 eV, 2.92 eV, and 2.67 eV, respectively. Thus, the dominant peak at 400 nm could be ascribed to the inter-bands PL phenomenon triggered by the light

with energy equals to the band gap energy of anatase TiO_2 while the peaks at 435 nm and 465 nm could be attributed to band edge free excitons (Yu and Ran 2011). The surface oxygen vacancies and defects of the electrospun TiO_2/CuO composite nanofibers could result in the excitonic PL as witnessed from weaker peaks between 470 nm and 500 nm (Yu and Ran 2011). The effect of Cu addition was clearly demonstrated by the significantly lower PL spectra than that of TiO_2 nanofibers. $\text{TiO}_2/\text{CuO(B)}$ is therefore expected to exhibit fast separation between photogenerated electrons and holes since lower PL spectra intensity indicates lower recombination tendency of the photogenerated charges (Ng, Xu et al. 2010). In the TiO_2/CuO heterojunctions, a different energy potential existed between the CB of TiO_2 and that of the CuO , thus promoting the migration of the photogenerated electrons from CB of TiO_2 to that of CuO and hence minimizing the recombination possibility of the photogenerated electrons and holes. Among all the TiO_2/CuO composite nanofibers, both $\text{TiO}_2/\text{CuO(B)}$ -1 and $\text{TiO}_2/\text{CuO(B)}$ -3 have the highest PL spectra, indicating their highest recombination tendency. This could be addressed by the relatively low Cu content in $\text{TiO}_2/\text{CuO(B)}$ -1 and $\text{TiO}_2/\text{CuO(B)}$ -3 which resulted in a weak effect of TiO_2/CuO heterojunctions in facilitating photogenerated charges separation. On the other hand, $\text{TiO}_2/\text{CuO(B)}$ -6, $\text{TiO}_2/\text{CuO(B)}$ -9, and $\text{TiO}_2/\text{CuO(B)}$ -12 possessed higher Cu content for the formation of TiO_2/CuO heterojunctions which promote transfer of the photogenerated charges.

Figure 5.8 Photoluminescence spectra of $\text{TiO}_2/\text{CuO(B)}$ -1, $\text{TiO}_2/\text{CuO(B)}$ -3, $\text{TiO}_2/\text{CuO(B)}$ -6, $\text{TiO}_2/\text{CuO(B)}$ -9, $\text{TiO}_2/\text{CuO(B)}$ -12 and TiO_2 nanofibers

The chemical composition of $\text{TiO}_2/\text{CuO(B)}$ was studied by XPS analysis. The results were observed in Figs. 5.9(a) – (d). The binding energy for C1s peak at 284.6 eV was used as the reference for calibration. The survey spectrum as presented in Fig. 5.9(a) confirms that only Ti, Cu, and O were present in $\text{TiO}_2/\text{CuO(B)}$, which are in consistent with the EDX spectrum. High resolution XPS spectrum of Ti 2p, Cu 2p, and O 1s were observed in Fig. 5.6(b) – (d), respectively. The peaks in the Ti 2p spectra (Fig. 5.9(b)) were indicative of Ti 2p_{3/2} and Ti 2p_{1/2} of Ti^{4+} (Liu, Sun et al. 2007, Lalitha, Sadanandam et al. 2010, Xu, Du et al. 2011), located at the binding energy of 458.0 eV and 464.0 eV, respectively. As shown in Fig. 5.9(c), the binding energy of 933.9 eV and 953.9 eV were ascribed to the Cu 2p_{3/2} and Cu 2p_{1/2} of Cu^{2+} in CuO (Wu and Lee 2004, Li, Dimitrijevic et al. 2008) respectively. The characteristic shakeup satellite peak around 942.0 eV and 962.0 eV further confirmed the oxidation state of Cu to be +2 (Córdoba, Viniegra et al. 1998, Li, Dimitrijevic et al. 2008, Shifu, Sujuan et al. 2009). The peak of O 1s spectrum (Fig. 5.9(d)) at binding energy of 529.5 eV was attributed to the O in TiO_2 and CuO (Wang, Shao et al. 2009, Xu, Du et al. 2011), whereas the peaks at higher binding energy of 531.2 eV was indicative of surface

contamination by hydroxides, from the atmosphere (Wang, Shao et al. 2009, Xu, Du et al. 2011).

h

Figure 5.9 (a) XPS survey spectrum for $\text{TiO}_2/\text{CuO(B)}$; High resolution XPS spectrum for (b) Ti 2p, (c) Cu 2p, and (d) O 1s

Base on the characterization results, $\text{TiO}_2/\text{CuO(B)}$ possessed an integration of beneficial physicochemical properties for photocatalysis, with higher specific surface area compared to that of $\text{TiO}_2/\text{CuO(A)}$, thus is expected to exhibit a more promising photocatalytic efficiency and stability.

5.3 Photocatalytic Efficiency of $\text{TiO}_2/\text{CuO(B)}$

Photocatalytic H_2 generation efficiency of $\text{TiO}_2/\text{CuO(B)}$ was evaluated using a 10% v/v methanol aqueous solution. TOC reduction was between 7-10% throughout the reaction for all $\text{TiO}_2/\text{CuO(B)}$. As illustrated in Fig. 5.10(a), an immense enhancement of H_2 production over the composite nanofibers in comparison to TiO_2 nanofibers and P25 was demonstrated. The amount of evolved

H₂ increased with increasing Cu content. The highest evolution occurred with 6% Cu sample, approximated to be 5800 µmol/hr. The enhanced physicochemical properties as discussed in Section 5.2 could have attributed to the enhanced photocatalytic efficiency of TiO₂/CuO(B). Figure 5.10(b) shows that photocatalytic H₂ generation was approximately 3 times higher using TiO₂/CuO(B)-6 than TiO₂/CuO(A). Compared to TiO₂/CuO(A), the enhanced pore volume and larger specific surface area of TiO₂/CuO(B)-6 as witnessed from the BJH and BET analysis in Fig. 5.5 and Table 5.1 respectively have increased the reaction sites availability thus facilitating reactants adsorption and interfacial charge transfer to the adsorbed substrates (Chen and Mao 2007, Chuangchote, Jitputti et al. 2009, Choi, Kim et al. 2010). In addition, smaller anatase TiO₂ crystal size as shown in Table 5.2 was advantageous because it offered shorter migration distance for photogenerated charge transfer to the surface reaction sites and thus lowered the recombination rate.

On the contrary, despite the enhanced BET specific surface area, mesoporosity, visible light absorption capability and photogenerated charges separation, the rate of H₂ generation removal showed a decreasing trend in TiO₂/CuO(B)-9 and TiO₂/CuO(B)-12 possibly due to the coverage of the host TiO₂ semiconductor by CuO which could limit the light accessibility thus limiting the initiation of photocatalytic reaction (Wang, Shao et al. 2009). In addition, the relatively higher crystalline defects of the anatase TiO₂ due to the higher Cu inclusion could contribute to the overall decrease in the photocatalytic H₂ generation by TiO₂/CuO(B)-9 and TiO₂/CuO(B)-12 because crystal defects are potentially charges recombination centers thus could retard the charges separation and subsequently weaken the photocatalytic performance (Pan, Dou et al. 2010). Overall, all TiO₂/CuO(B) have exhibited higher H₂ generation compared to TiO₂/CuO(A) ascribing to enhanced porosity and specific surface area in TiO₂/CuO(B).

Figure 5.10 (a) Photocatalytic H_2 evolution rate of P25, TiO_2 , $\text{TiO}_2/\text{CuO(A)}$ and all $\text{TiO}_2/\text{CuO(B)}$ in 10% v/v methanol under UV-visible light irradiation; and (b) Comparison of photocatalytic H_2 evolution between $\text{TiO}_2/\text{CuO(B)-6}$ and $\text{TiO}_2/\text{CuO(A)}$ under UV-visible light irradiation in 10% v/v methanol.

5.4 Mechanism

Mechanism of photocatalytic H_2 and clean water generation in $\text{TiO}_2/\text{CuO(B)}$ is postulated to be similar to that of $\text{TiO}_2/\text{CuO(A)}$ owing to the chemistry nature of the TiO_2/CuO heterojunction. The high H_2 evolution was corroborated to the Cu in the

heterojunctions which functions as the electron accumulation and H_2 reduction site. Figure 5.11 elucidates the electrons and holes transfer pathway within $\text{TiO}_2/\text{CuO(B)}$. The energy difference between the CB of both semiconductors favors the transfer of photogenerated electrons from TiO_2 to CuO upon absorption of photon (Helaïli, Bessekhoud et al. 2009). Accumulation of electrons in the CB of CuO resulted in a negative shift of the potential which facilitated the fast interfacial electron transfer (Jin, Zhang et al. 2007). Consequently, recombination of photogenerated electrons and holes was impeded and H_2 evolution efficiency was enhanced. Additionally, the onset of the red-shift as observed by the UV-vis absorption spectra also enhanced the photoresponse and electron-hole pair's photo-generation capability of the composite nanofibers to initiate the photocatalytic reaction. An efficient electron transfer and charge separation (Li and Xia 2004) within the long 1D nanofibrous structure could further inhibit the electron-hole recombination (Choi, Kim et al. 2010) while promoting the availability and lifetime of the active species for photocatalytic reaction. The photogenerated holes left in the VB of $\text{TiO}_2/\text{CuO(B)}$ are easily scavenged for oxidation of methanol in the solution (Xu and Sun 2009).

Figure 5.11 Schematic diagram of the photo-generated electrons and holes transfer in the TiO_2/CuO composite nanofibers (NHE = Normal Hydrogen Electrode)

5.5 Summary

TiO₂/CuO composite nanofibers (TiO₂/CuO(B)) possessing novel integration of beneficial physicochemical properties as follows were successfully fabricated for the first time via electrospinning an innovated precursor solution.

- Consistent and long nanofibrous structure composed of granular nanocrystals, with high aspect ratio. This promotes interparticle charge transfer along the long nanofibrous structure,
- Smaller anatase TiO₂ crystal size promoted by the Cu loading is advantageous because it renders higher contact area with TiO₂ as well as shorter migration distance for photogenerated charge transfer to the surface reaction sites and thus lowers the recombination rate.
- Highly dispersed Cu in respective composite nanofibers which ensure good contact between TiO₂ and CuO, serves to enhance the photogenerated electrons and holes transfers between the heterojunctions.
- Increased porosity and specific surface area promotes light absorption and utilization; and reactants adsorption; thus facilitating mass transfer and interfacial charge transfer for an efficient heterogeneous photocatalysis.
- Red-shift of the composite nanofibers extends the photocatalysts' ability to utilize the light energy source from UV range into visible range.
- Minimized recombination rate of photogenerated electrons and holes owing to the heterojunctions formed in the composite nanofibers, thus promoting the charge migration and separation.

The optimum Cu content that facilitated the best photocatalytic H₂ generation over TiO₂/CuO(B) was determined to be 6 % mol (TiO₂/CuO(B)-6). Due to the nature of the precursor solution preparation which entailed mixing of chemicals at the molecular level, TiO₂/CuO(B) could be synthesized without compromising the specific surface area of TiO₂ nanofibers, while enhancing the beneficial physicochemical properties of 1D nanofibrous structure, unlike that in Approach A

or other conventional methods such as wet-impregnation. The uniform distribution and high dispersion of CuO achieved on the surface and bulk of the host semiconductor (TiO₂) instead of just the surface (Xu and Sun 2009, Xu, Ng et al. 2010, Xu, Du et al. 2011), coupled with the enhanced mesoporosity would facilitate greater accessibility of the reactants to the TiO₂-CuO heterojunction, thus enhancing the overall photocatalytic H₂ generation efficiency of TiO₂/CuO(B).

CHAPTER 6 APPLICATION PROSPECTS AND STABILITY OF TiO₂/CuO(A) AND TiO₂/CuO(B)

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6.1 Introduction

As an approach to enhance environmental sustainability of TiO₂ photocatalysis, electrospinning has been successfully exploited for its simplicity and versatility as demonstrated in Chapter 4 and 5. The unique physicochemical properties of electrospun nanofibers have been shown to benefit photocatalytic efficiency of TiO₂ to harvest both clean water and H₂. Approach A, while exhibiting an ingenious integration of Cu-EDTA waste water and 1D TiO₂ nanofibers to co-generate H₂ and clean water efficiently and sustainably via photocatalysis, has paved a green synthesis route for TiO₂/CuO composite which possess a good potential for co-generation of photocatalytic H₂ and clean water. It represents an adoptable approach to synthesize TiO₂/CuO composite nanofibers in a more sustainable way, despite the reduced specific surface area. Meanwhile, Approach B offers a facile option to synthesize novel-structured TiO₂/CuO composite nanofibers with good photocatalytic efficiency through one-step electrospinning of an innovated precursor solution for the first time, without compromising the unique

physicochemical properties of the nanofibrous structure. Instead, Approach B produced composite nanofibers comprising the synergy of enhanced physicochemical properties. Both approaches were novel and offer procedural and resource simplicity, unlike the conventional synthesis methods. Most importantly, they represent significant advancement in TiO_2 photocatalysis for simultaneous H_2 and clean water production, especially in the fundamental of green chemistry and environmental sustainability research domains. Moving forward, the application prospect of both $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ to co-generate H_2 and clean water from different waste water models such as Acid Orange 7 (AO7) and glycerol, were discussed in this chapter. $\text{TiO}_2/\text{CuO(B)}$ -6 will be used as it was found to be the optimum in Chapter 5. The stability of $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ as were also explored to determine application and optimization opportunity.

6.2 Photocatalytic co-generation of H_2 and clean water from waste water by $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$

6.2.1 Acid orange 7 (AO7)

Photocatalytic organic degradation by $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ were evaluated by means of its discoloration efficiency in a 20 mg/L AO7 solution irradiated with UV-visible light and thereafter compared with that of the as-prepared TiO_2 nanofibers under the same experimental condition. Following a 30-min dark adsorption process, the suspension was subjected to photocatalytic reaction for 3 hours. Figure 6.1 illustrates the changes in concentration of AO7 when $t=3$ min during the UV-visible irradiation.

Figure 6.1 Removal of AO7 by PCO at $t=3$ minutes during the UV-visible irradiation on the photocatalysts suspension

Discoloration of AO7 as illustrated in Fig. 6.1 was enhanced by photocatalysis in the presence of TiO₂/CuO(B) or TiO₂/CuO(A), hence indicating the prominent role played by the photocatalysts in promoting the degradation rate of the organic pollutant from waste water. Complete discoloration of the dye solution due to photocatalysis was observed in less than 20 min in the presence of photocatalyst, whereas under photolysis (without photocatalyst) a longer duration of approximately 40 min was required to remove the colour of the dye solution with the same concentration. Discoloration of the AO7 solution was ascribed to the breaking of azo-bond of AO7 into smaller colorless molecules upon oxidation by the photogenerated holes and holes-induced ROS such as OH $\cdot$ on the surface reactive sites and bulk solution, respectively (Stylidi, Kondarides et al. 2004). TiO₂/CuO(B) demonstrated the highest discoloration of 35.3 % at $t=3$ min during the irradiation. Meanwhile, TiO₂/CuO(A) showed a lower discoloration of 30.0% at $t=3$ min possibly owing to the lower specific surface area and pore volume which limit direct access and adsorption of reactants or intermediate by-products. Overall, the enhanced photocatalytic organic degradation over both TiO₂/CuO(A) and TiO₂/CuO(B) was ascribed to: (1) the TiO₂/CuO heterojunctions which have retarded the recombination of the photogenerated holes and electrons, as verified by

the PL emission in Fig.4.12 and 5.8 and (2) the red-shift of absorbance spectra as witnessed by the UV-vis spectra in Fig. 4.11 and 5.7 thus increasing the light utilization ability. The highly dispersed Cu in the composite nanofibers as well-witnessed in the elemental mapping in Fig. 4.8 and 5.4 also suggested that good contact between TiO_2 and CuO , which further enhanced the photogenerated electrons and holes separation between the heterojunctions. As presented in Fig. 6.2, H_2 evolution rate over $\text{TiO}_2/\text{CuO(B)}$ was approximately 1.5 times higher than that of $\text{TiO}_2/\text{CuO(A)}$.

Figure 6.2 Photocatalytic H_2 generation and TOC removal from 20 mg/L AO7 over $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ under UV-visible light irradiation

Relatively negligible H_2 was generated in the absence of either photocatalyst or light (data not shown) as well as in the presence of TiO_2 nanofibers (data not shown). Despite the complete discoloration of AO7 solution in less than 20 min, H_2 was continuously generated throughout reaction because complete mineralization of AO7's intermediate oxidation by-products into H_2O and CO_2 required a much longer time (Patsoura, Kondarides et al. 2006). This verifies the theory that H_2 will be generated via H_2O reduction by photogenerated electrons as long as the recombination of the electron-hole pairs and the back reaction of H_2 and O_2 were retarded by photo-oxidation of organic molecule by the photogenerated holes (Kudo and Miseki 2009). The enhanced generation of H_2 over the composite nanofibers

was attributed mainly to the synergy effect of the excellent physicochemical properties such as (1) enhanced mesoporosity and specific surface area for the case of $\text{TiO}_2/\text{CuO(B)}$, (2) red-shift of the solar light absorbance and (3) TiO_2/CuO heterojunctions, which ultimately promote charge transfer and separation as well as enhance light utilization. The composite's enhanced efficiency become even more significant by the diminishing effect of dye-sensitization following the complete discoloration of AO7 solution in the first half an hour of the reaction since H_2 generation continued to rise thereafter. Meanwhile, $\text{TiO}_2/\text{CuO(B)}$ and $\text{TiO}_2/\text{CuO(A)}$ demonstrated H_2 evolution rate which is nearly 3 times and 1.5 times higher respectively than the rate obtained with the Pt/TiO_2 nanoparticles (Patsoura, Kondarides et al. 2006). This implies that Cu can be a potential substitute to Pt in the modification of TiO_2 properties for concurrent photocatalytic organic degradation and H_2 production from dye wastewater.

The enhancement of photocatalytic organic degradation by dye-sensitization phenomenon of TiO_2 by the adsorbed AO7 has been well-studied and can be found elsewhere (Tanaka, Padernpole et al. 2000, Stylidi, Kondarides et al. 2004). Dye-sensitization of TiO_2 leads to utilization of the visible light and thus more formation of ROS which eventually enhance the total photocatalytic degradation of dye. However, dye-sensitization is very much dependent on the continuous supply of colored dye wastewater because the colorless by-products from the degradation of AO7 was not sensitive towards visible light (Stylidi, Kondarides et al. 2004). Since a batch reactor was employed in this study, it is therefore reasonable to conclude that the contribution by dye-sensitization was only valid in the first half an hour of the degradation process. Thus, the physicochemical properties of $\text{TiO}_2/\text{CuO(B)}$ and $\text{TiO}_2/\text{CuO(A)}$ still play a big role in enhancing the overall photocatalytic organic degradation and H_2 generation process.

6.2.2 Glycerol

Both $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ were also tested for their photocatalytic function to co-generate H_2 and clean water generation from glycerol, a primary

waste product from the biodiesel production industry (Yu and Ran 2011). Concurrent photocatalytic H₂ generation and TOC removal from 5% v/v glycerol over TiO₂/CuO(A) and TiO₂/CuO(B) were illustrated in Fig. 6.3.

Figure 6.3 Photocatalytic H₂ generation and TOC removal from 5% v/v glycerol over TiO₂/CuO(A) and TiO₂/CuO(B) under UV-visible light irradiation

The mechanism involved in the photocatalytic treatment of glycerol using TiO₂ to cogenerate H₂ and clean water has been extensively proposed elsewhere (Lalitha, Sadanandam et al. 2010, Yu and Ran 2011). Both TiO₂/CuO(A) and TiO₂/CuO(B) exhibited comparably efficient H₂ generation rate of approximately 2627 μmol/hr and 2647 μmol/hr, respectively under UV-visible light. The synergy between all the enhanced physicochemical properties of TiO₂/CuO(A) and TiO₂/CuO(B) could have driven the net photocatalytic reaction despite the reduced specific surface area in TiO₂/CuO(A) (Lee, Bai et al. 2013). On the other hand, TOC removal was higher in TiO₂/CuO(B) owing to its superior specific surface area and porosity compared to TiO₂/CuO(A). Meanwhile, the higher Cu deposition (approximately 22.7% mol) on TiO₂/CuO(A) could be one of the factors limiting the light absorption efficiency and activation by TiO₂. Overall, both TiO₂/CuO(A) and TiO₂/CuO(B) exhibited good H₂ generation with approximately 10% TOC removal.

TiO₂/CuO(A) and TiO₂/CuO(B) were both tested for their H₂ generation from 5%v/v glycerol under the visible light. As depicted in Fig. 6.4, both showed encouraging H₂ generation rate of 562.0 $\mu\text{mol/hr}$ for TiO₂/CuO(B) and 407.1 $\mu\text{mol/hr}$ for TiO₂/CuO(A), suggesting a more sustainable feature where more of the renewable solar irradiation could be exploited.

Figure 6.4 Photocatalytic H₂ generation from 5%v/v glycerol over TiO₂/CuO(A) and TiO₂/CuO(B) under UV-visible and visible lights irradiation

6.3 Stability and reusability of TiO₂/CuO(A) and TiO₂/CuO(B)

The prospect of recovery and reusability of a photocatalyst is one of the crucial factors in determining the viability of using the photocatalyst for water treatment. Unrecoverable photocatalyst after a treatment process may result in a secondary pollution of the effluent water thus posing potential threat to human health and that of the ecosystem. Repeated use of TiO₂/CuO(A) and TiO₂/CuO(B) were feasible owing to their sustainable 1D long nanofibrous structure which thus have enabled the ease of recovery and reuse; further corroborated by the FESEM images (Fig. 6.5) showing the unchanged morphology of the repeatedly used TiO₂/CuO(A) and

TiO₂/CuO(B). The specific surface area could be easily recovered via facile calcinations at 450 °C overnight.

Figure 6.5 FESEM-STEM image of TiO₂/CuO(A) which has been used for reaction in 5% v/v glycerol and regenerated via calcinations (a) low magnification and (b) high magnification, FESEM-STEM image of TiO₂/CuO(B) which has been used for reaction in 5% v/v glycerol and regenerated via calcinations (c) low magnification and (d) high magnification

As shown in Figs. 6.6, reduction in photocatalytic H₂ generation was negligible when TiO₂/CuO(A) and TiO₂/CuO(B) were recycled for use in AO7 and glycerol respectively. Moreover, Cu²⁺ ion was constantly below the detection limit of 1.0 mg/L in the reacting solution after every cycle, complying with the industrial wastewater effluent standard for Cu as specified by the US EPA (Chen, Chai et al. 2012). Photocatalytic H₂ generation was lower from AO7 than that from glycerol possibly due to the relatively bulkier and more complex molecular structure of AO7 compared to glycerol (Fig. 6.7). During the reaction in this study, compared to

glycerol, AO7 and its intermediates could have occupied relatively more surface reaction sites or covered a larger surface area of photocatalyst; thus possibly interfered with the electron transfer on the surface of the photocatalyst for water molecule reduction to generate H_2 .

Figure 6.6 Reusability experiment for photocatalytic H_2 generation by $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ in (a) AO7 under UV-visible light, and (b) 5% v/v glycerol under UV-visible and visible lights

Figure 6.7 Molecular structure of (a) AO7, and (b) glycerol

Table 6.1 shows the leachability of Ti and Cu from TiO₂/CuO(A) and TiO₂/CuO(B) in different medium, with DI water as the standard. In general, both TiO₂/CuO(A) and TiO₂/CuO(B) exhibited comparable leachability under all medium, with the exception of higher Cu leaching at pH 2 from TiO₂/CuO(A). This could be attributed to the Cu agglomerates on TiO₂/CuO(A) resulted from its synthesis nature especially when TiO₂/CuO(A) was composed of higher Cu content to begin with. On the other hand, TiO₂/CuO(B) exhibited approximately 2 times lower Cu leaching possibly ascribing to its fabrication method which could have rendered the TiO₂/CuO(B) with a greater stability. The employed electrospinning of innovative precursor has enabled an optimized chemical usage where good elemental contact and high dispersion hence minimizing agglomeration of Cu elements within TiO₂/CuO(B). Consequently, Cu leaching was minimized from TiO₂/CuO(B) as it could be strongly held within the matrix of host TiO₂ photocatalyst (Xu, Ng et al. 2010). It is postulated that the higher H₂ generation and TOC removal from waste water model over TiO₂/CuO(B) (Figs. 6.1, 6.2 and 6.3) was also ascribed to the more superior stability of TiO₂/CuO(B). With the detection of less than 1.0 mg/L for both Ti and Cu, glycerol was shown to be a potentially ideal candidate in this study for treatment by TiO₂/CuO(A) and TiO₂/CuO(B) to harvest H₂ and clean water.

Table 6.1 Summary of leachability of Ti and Cu from photocatalysts

Photocatalyst	Medium	Ti (mg/L)	Cu (mg/L)
TiO ₂ /CuO(B)	DI water	0.019	0.278
	Diluted NaOH (pH 12)	0.880	0.089
	Diluted HNO ₃ (pH 2)	0.386	16.75
	5% v/v Glycerol	0.008	0.836
TiO ₂ /CuO(A)	DI water	0.000	0.462
	Diluted NaOH (pH 12)	1.474	0.135
	Diluted HNO ₃ (pH 2)	0.376	33.68
	5% v/v Glycerol	0.004	0.538

6.4 Summary

TiO₂/CuO(A) and TiO₂/CuO(B) exhibited significant potential to concurrently evolve H₂ and degrade common organic pollutants such as AO7 and glycerol. Both could exploit the renewable solar energy to harvest H₂ and clean water from waste water. Nevertheless, TiO₂/CuO(B) showed a relatively more superior chemical stability possibly owing to its the synthesis nature which has endowed TiO₂/CuO(B) with chemically stronger TiO₂/CuO₂ heterojunctions as well as the higher Cu composition on TiO₂/CuO(A). In essence, both photocatalysts possessed sufficient physical and chemical stability for an efficient photocatalysis in environmental application.

CHAPTER 7 STUDY ON PHYSICOCHEMICAL PROPERTIES-PHOTOCATALYTIC EFFICIENCY RELATIONSHIP AND OPTIMIZATION OF ELECTROSPUN TiO₂/CuO COMPOSITE

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7.1 Introduction

Chapter 6 has shown that both TiO₂/CuO(B) and TiO₂/CuO(A) were capable for harvesting H₂ while degrading common industrial organic pollutants via photocatalysis. TiO₂/CuO(B) offered better stability thus photocatalytic efficiency owing to the principle of Approach B which emphasized on mixing the precursor for both Ti and Cu at the molecular level prior to electrospinning, facilitating a stable incorporation of Cu within the matrix of TiO₂. Nevertheless, the feasibility of using TiO₂/CuO(B) in acidic medium could be limited due to the leachability of Cu. In this chapter, an in-depth study on the relationship between physicochemical properties and photocatalytic efficiency was undertaken and addressed in search for an optimization opportunity for TiO₂/CuO(B) to extend its operational pH range as well as to build on the fundamental science for TiO₂/CuO(B).

7.2 Effect of calcinations temperature on physicochemical properties

TiO₂/CuO(B)-6 was utilized in this study since it exhibited incorporation of beneficial physicochemical properties for a good photocatalytic efficiency in Chapter 5. TGA was first performed on the uncalcined as-spun PVP/Ti(oBu)₄/

$\text{Cu}[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2$ composite nanofibrous mat to determine the thermal stability of the photocatalyst prior to calcinations. Figure 7.1 illustrated the TGA curve of $\text{TiO}_2/\text{CuO(B)}\text{-6}$ in the air across a range of 25 °C-800 °C with temperature increase rate of 5 °C/min. Three distinctive phases of weight loss could be deduced: 1) Between 25 °C-100 °C - Loss of moisture adsorbed by the as-spun nanofibrous web from the atmosphere (Wu 2007), 2) Between 100 °C-300 °C - Loss of water molecules originated from the chemicals used and throughout the synthesis process (Wu 2007), and 3) Between 300 °C-450 °C - Loss of polymer and organic (Wu 2007). No further weight loss was observed from 450 °C-800 °C. The TGA curve was the basis from which the calcinations temperatures of investigation were determined.

Figure 7.1 TGA curve for uncalcined $\text{TiO}_2/\text{CuO(B)}\text{-6}$

Prior to relating the physicochemical properties and the H_2 generation activity, the influence of calcinations temperature on physicochemical properties were first identified and clarified. Figure 7.2(a)-(e) illustrates the FESEM images which clarified the surface morphology of the photocatalysts. While no significant temperature effect on the surface morphology was observed in a report by Wu J. (2007) on pristine TiO_2 nanorods (Wu 2007), in this study, the FESEM images vividly showed that as the calcinations temperature increases, the surface of the

TiO₂/CuO composite nanofibers have evolved from a non-porous surface structure (Fig. 7.2(a)), into a very rough and porous surface (Fig. 7.2(b)-(c)), and finally into a smooth-surfaced structure with diminishing porosity (Fig. 7.2(d)-(e)). Higher temperature could promote fusion and growth of the granular nanocrystals into larger crystals (Wu 2007) thus possibly resulting in a smoother surface structure. Figure 7.3 shows the HRTEM microstructure images of the composite, further evidenced the diminishing porosity and enlarged crystalline structure with increased calcinations temperature. Nevertheless, the overall morphology remained long regardless of the calcinations temperature.

Figure 7.2 High magnification -FESEM images for (a) TiO₂/CuO(B)-350, (b) TiO₂/CuO(B)-450, (c) TiO₂/CuO(B)-550, (d) TiO₂/CuO(B)-650, and (e) TiO₂/CuO(B)-750

Figure 7.3 HRTEM images for (a) $\text{TiO}_2/\text{CuO(B)}$ -350, (b) $\text{TiO}_2/\text{CuO(B)}$ -450, (c) $\text{TiO}_2/\text{CuO(B)}$ -550, (d) $\text{TiO}_2/\text{CuO(B)}$ -650, and (e) $\text{TiO}_2/\text{CuO(B)}$ -750

The increase of calcinations temperature has resulted in an enhanced degree of crystallization as evidenced by the growingly sharpening peaks of the XRD patterns (Wu 2007) as illustrated in Fig. 7.4, which was further affirmed by the narrowing of full width at half maximum (FWHM) with elevating temperature as shown in Table 7.1.

Figure 7.4 XRD patterns of $\text{TiO}_2/\text{CuO(B)}$ -350, $\text{TiO}_2/\text{CuO(B)}$ -450, $\text{TiO}_2/\text{CuO(B)}$ -550, $\text{TiO}_2/\text{CuO(B)}$ -650, and $\text{TiO}_2/\text{CuO(B)}$ -750 nanofibers

Table 7.1 Summary of crystal size for TiO₂/CuO(B)-6 at different calcinations temperature

Photocatalyst	FHWM (degree)	Size of anatase crystal ^a (nm)
TiO ₂	0.443	18.2
TiO ₂ /CuO(B)-350	0.450	17.0
TiO ₂ /CuO(B)-450	0.493	16.4
TiO ₂ /CuO(B)-550	0.319	25.3
TiO ₂ /CuO(B)-650	0.249	32.4
TiO ₂ /CuO(B)-750	0.176	45.8

^a Calculated by the Scherrer equation (Chen and Mao 2007, Ohtani 2008).

Good crystallinity is essential to ensure minimum defects within the crystal structure thus ensuring fast separation of photogenerated charges (Kudo and Miseki 2009). In addition to anatase TiO₂ phase (JCPDS file No. 21-1272) (Liu, Sun et al. 2007), peaks corresponding to rutile TiO₂ and CuO started to appear at 450 °C and beyond. Additional Cu₂O phase on top of rutile TiO₂ and CuO was obvious in the XRD pattern of TiO₂/CuO(B)-750. The most intensified peaks for rutile TiO₂ (JCPDS file No. 21-1276) (Liu, Sun et al. 2007), CuO (JCPDS file No.48-1548) (Mor, Varghese et al. 2008) and Cu₂O (JCPDS file No. 74-1230) (Yu, Yu et al. 2007) were located at $2\theta = 37^\circ$ (101), 38.8° (002), and 36.5° (111), respectively. In addition to greyish and blackish shades, TiO₂/CuO(B)-550, TiO₂/CuO(B)-650, and TiO₂/CuO(B)-750 nanofibers exhibited increasing intensity of red shade as temperature increases suggested the existence of CuO and Cu₂O in the photocatalysts. Higher temperature could induce the phase transformation of CuO into Cu₂O as Cu²⁺ was reduced to Cu⁺ (Yu, Yu et al. 2007). Similar observation was also reported by Lalitha et al (2010) where CuO and Cu₂O were formed at low and high calcinations temperature, respectively (Lalitha, Sadanandam et al. 2010). Nonetheless, Wu et al (2009) demonstrated an opposite phenomenon whereby CuO was synthesized at 450 °C and beyond (Wu, Lu et al. 2009). Different synthesis conditions, routes and chemicals employed could possibly address the discrepancies observed in the resulting photocatalysts. Meanwhile, based on the Scherrer

equation, the crystal size was found to increase with the temperature (Table 7.1), with the highest being that of TiO₂/CuO(B)-750 which was approximated to be 45.8 nm. This estimated trend was consistent with the observed morphology using HRTEM in Fig. 7.3(a)-(e) whereby the granular nanocrystals were enlarged thus resulting in a smoother surface at higher temperature.

A report by Bueno-Ferrer et al (2010) demonstrated that larger crystals exhibit lower specific surface area (Bueno-Ferrer, Parres-Esclapez et al. 2010). Likewise in this study, TiO₂/CuO(B)-750 had the least specific surface area as well-corroborated by the measured BET specific surface area as depicted in Table 7.2. Both TiO₂/CuO(B)-450 and TiO₂/CuO(B)-550 have the highest specific surface area, implying enhanced adsorption capability for mass transfer. Meanwhile, the N₂ adsorption-desorption isotherm technique showed that TiO₂/CuO(B)-350 was not mesoporous (Fig. 7.5(a)), which was in good agreement with the rather smooth surface morphology as shown in Fig. 7.2(a) and Fig. 7.3(a). Since PVP removal under high temperature is one of the contributing factors for porosity formation (Li and Xia 2003), the presence of polymer at 350°C as witnessed by the TGA curve in Fig. 7.1 could address the incomplete transformation of the nanofibers with porous structure hence yielding a smooth surface.

Table 7.2 Summary of BET specific surface area for TiO₂/CuO(B) at different calcinations temperature

Photocatalyst	BET specific surface area (m ² /g)
TiO ₂	34.30
TiO ₂ /CuO(B)-350	73.78
TiO ₂ /CuO(B)-450	156.22
TiO ₂ /CuO(B)-550	120.40
TiO ₂ /CuO(B)-650	43.42
TiO ₂ /CuO(B)-750	17.85

Disappearance of mesoporosity was also observed in $\text{TiO}_2/\text{CuO(B)}-650$ and $\text{TiO}_2/\text{CuO(B)}-750$ due to the growth of crystals which has diminished the pores. This was clearly illustrated in Figs. 7.2 and 7.3 and thus also addressed the decreasing specific surface area from $\text{TiO}_2/\text{CuO(B)}-350$ to $\text{TiO}_2/\text{CuO(B)}-750$ (Table 2). Only both $\text{TiO}_2/\text{CuO(B)}-450$ and $\text{TiO}_2/\text{CuO(B)}-550$ were mesoporous. Hence, specific surface area of $\text{TiO}_2/\text{CuO(B)}-350$ could be endowed by its large aspect ratio, while the significantly high specific surface area of $\text{TiO}_2/\text{CuO(B)}-450$ and $\text{TiO}_2/\text{CuO(B)}-550$ were possibly given by the enhanced mesoporosity coupled with the large aspect ratio. Mesoporous structures also play an important role in facilitating fast diffusion of reactants to enhance the photocatalytic reaction (Pan, Sun et al. 2010). Fig. 7.5(b) shows the pore size distributions of $\text{TiO}_2/\text{CuO(B)}-6$ calcined at different temperatures. Unlike $\text{TiO}_2/\text{CuO(B)}-450$ and $\text{TiO}_2/\text{CuO(B)}-550$ which possessed larger pore size of between 6 - 12 nm, $\text{TiO}_2/\text{CuO(B)}-350$, $\text{TiO}_2/\text{CuO(B)}-650$ and $\text{TiO}_2/\text{CuO(B)}-750$ exhibited smaller pore size peaking at 3 nm thus further corroborating the absence of mesoporosity (Fig. 7.5(a)) due to the incomplete formation of porous nanofibers in $\text{TiO}_2/\text{CuO(B)}-350$ as well as the enhanced crystal growth at higher calcinations temperature in $\text{TiO}_2/\text{CuO(B)}-650$ and $\text{TiO}_2/\text{CuO(B)}-750$ (Wu 2007).

Figure 7.5 (a) N₂ adsorption/desorption isotherm curve of TiO₂/CuO(B)-6 calcined at different temperatures, and (b) BJH pore size distributions of TiO₂/CuO(B)-6 calcined at different temperatures.

The XPS analysis was employed to determine the chemical states of all the elements in TiO₂/CuO(B)-6 calcined at different temperatures, in particular Ti and Cu. The binding energy for C1s peak at 284.6 eV was used as the reference for calibration. Figure 7.6(a) is the typical survey spectrum by TiO₂/CuO(B)-450 and it confirms that Ti, Cu, and O were present in the composite nanofibers.

Figure 7.6 (a) XPS survey spectrum for $\text{TiO}_2/\text{CuO(B)}$ -450 nanofibers; High resolution XPS spectrum for $\text{TiO}_2/\text{CuO(B)}$ -450 for (b) Ti 2p and (c) O 1s, and (d) High resolution XPS spectrum for $\text{TiO}_2/\text{CuO(B)}$ -6 at different calcinations for Cu 2p

The valence state for Ti remained +4 for all photocatalysts as evidenced by the peaks at the binding energy of 458.0 eV and 464.0 eV which were indicative of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively (Fig. 7.6(b)). Meanwhile, as shown in Fig. 7.6(c), the peaks at binding energy of 529.5 eV was the evidence of O 1s in TiO_2 and CuO or Cu_2O (Xu, Du et al. 2011). A high resolution spectrum for Cu 2p in Fig. 7.6(d) implies that the valence state of Cu could have been changed with temperature. $\text{TiO}_2/\text{CuO(B)}$ -350, $\text{TiO}_2/\text{CuO(B)}$ -450 and $\text{TiO}_2/\text{CuO(B)}$ -550 exhibited peaks around the binding energy of 933.9 eV and 953.9 eV ascribing to the Cu 2p_{3/2} and Cu 2p_{1/2} of Cu^{2+} in CuO (Wu and Lee 2004), respectively. The obvious characteristic shakeup satellite peaks around 942.0 eV and 962.0 eV further confirmed the existence of Cu^{2+} in $\text{TiO}_2/\text{CuO(B)}$ -350, $\text{TiO}_2/\text{CuO(B)}$ -450 and $\text{TiO}_2/\text{CuO(B)}$ -550 (Li, Dimitrijevic et al. 2008). On the other hand, in $\text{TiO}_2/\text{CuO(B)}$ -650 and $\text{TiO}_2/\text{CuO(B)}$ -750, despite the presence of peak at 933.9 eV

and its shakeup peaks at 942.0 eV, the peak at 953.9 eV with its corresponding shakeup peaks at 962.0 eV have weakened. Based on the XRD pattern in Fig. 7.4 and the reddish shade of the photocatalysts, the co-presence of Cu^+ and Cu^{2+} might be the reasonable cause for the diminishing Cu^{2+} peaks at high temperature for $\text{TiO}_2/\text{CuO(B)}-650$ and $\text{TiO}_2/\text{CuO(B)}-750$ despite no obvious XPS peak was observed for Cu^+ possibly due to its low content (Su, Shen et al. 2007, Wu, Lu et al. 2009). The valence state of Cu element may result in a different photocatalytic performance of the TiO_2/CuO composite nanofibers (Yu, Yu et al. 2007).

7.3 Interplay between physicochemical properties on photocatalytic activity

Figure 7.7 clearly illustrates the effect of calcinations temperature thus the influence of physicochemical properties on photocatalytic H_2 generation.

Figure 7.7 Dependence of H_2 evolution rate on the calcinations temperature in photocatalysts

$\text{TiO}_2/\text{CuO(B)}-450$ appeared to be the most efficient among others, with the highest H_2 generation rate of $5800 \mu\text{mol/hr}$. Incorporated with the high magnification FESEM images of $\text{TiO}_2/\text{CuO(B)}-350$, $\text{TiO}_2/\text{CuO(B)}-450$, $\text{TiO}_2/\text{CuO(B)}-550$, $\text{TiO}_2/\text{CuO(B)}-650$, and $\text{TiO}_2/\text{CuO(B)}-750$, an overview of how the physicochemical properties have changed with the calcinations temperature was given in Fig. 7.8 in

order to vividly illustrate the interdependency between physicochemical properties for H₂ generation.

Figure 7.8 Schematic of the effect of calcinations temperatures on the physicochemical properties

TiO₂/CuO(B)-450 possesses beneficial integration of (1) mesoporosity with high specific surface area which enables high reactants accessibility, diffusion and adsorption, (2) good crystallinity thus minimum defects for efficient charge transfer, (3) enhanced light absorption capability thus facilitating photogeneration of charges, as well as (4) crystal size small enough to promote accessibility of the surface reaction sites by the photogenerated charges (Pan, Dou et al. 2010). On the contrary, TiO₂/CuO(B)-550, regardless being comparable with TiO₂/CuO(B)-450 in terms of mesoporosity, specific surface area, and light absorption capability, exhibited better crystallinity thus resulting in a larger crystal size (Table 7.1). Even though good crystalline structure is favourable for charges transfer (Pan, Dou et al.

2010), the large crystal size may be detrimental to the overall photocatalytic performance due to the longer migration distance that needed to be overcome by the photogenerated charges in order to reach the surface reaction sites. Moreover, TiO₂/CuO(B)-550 has less mesopores volume (Fig. 7.5(a)) compared to TiO₂/CuO(B)-450 thus has less efficient mass transfer through the photocatalysts which could limit the photocatalytic reaction (Pan, Sun et al. 2010).

The importance of a good synergy between major physicochemical properties as exhibited in TiO₂/CuO(B)-450 become more significant when both TiO₂/CuO(B)-650 and TiO₂/CuO(B)-750 demonstrated remarkably lower H₂ generation efficiency than that of TiO₂/CuO(B)-450 and TiO₂/CuO(B)-550 due to the negative effects from the small specific surface area, large crystal size and absence of mesoporosity which has dominated the enhanced charge transfer efficiency effect from the higher degree of crystallinity. Likewise, TiO₂/CuO(B)-350 which was not mesoporous with low crystallinity, exhibited the least photocatalytic efficiency because lacked adsorption, diffusivity and charge transfer efficiency albeit possessing small crystal size. Meanwhile, the higher H₂ generation rate over TiO₂/CuO(B)-750 compared to TiO₂/CuO(B)-350 suggested that degree of crystallinity could be a more dominant factor than specific surface area in driving the photocatalytic H₂ generation. However, since the synergy of more than one physicochemical properties determines the overall photocatalytic efficiency, there would be a limit where a much higher degree of crystallinity at the expense of excessive specific surface area could retard the final H₂ generation efficiency, such as that seen in TiO₂/CuO(B)-750 compared to TiO₂/CuO(B)-650. While Cu₂O has been reported to be the active site for photocatalytic H₂ generation (Wu, Lu et al. 2009, Lalitha, Sadanandam et al. 2010, Xu, Ng et al. 2010), the presence of Cu₂O alone may not be sufficient in enhancing the overall photocatalytic performance as observed in TiO₂/CuO(B)-550, TiO₂/CuO(B)-650 and TiO₂/CuO(B)-750 owing to the absence of other positive factors in particular optimum specific surface area, mesoporosity, and appropriate crystal size. This study suggested that CuO is also an active reaction site and does not inhibit photocatalytic H₂ generation as that reported before (Wu, Lu et al. 2009)

since CuO was solely observed in TiO₂/CuO(B)-450 (Fig. 7.4 and Fig. 7.6(d)) which exhibited the highest photocatalytic capability.

The photocatalytic H₂ generation efficiency over TiO₂/CuO(B) under sole visible light was also investigated to bolster the value of TiO₂/CuO(B) as prospective photocatalysts for renewable clean energy fuel and clean water production. TiO₂/CuO(B)-450 and TiO₂/CuO(B)-750 were used for this study owing to the different dominance of CuO and Cu₂O which have different bandgap energies (Helaïli, Bessekhoud et al. 2009) and both photocatalysts possessed the extreme characteristics and properties of both ends (Fig. 7.8). Negligible H₂ generation was observed when TiO₂ nanofibers were used under the visible light irradiation. As depicted in Fig. 7.9, both TiO₂/CuO(B)-450 and TiO₂/CuO(B)-750 exhibited encouraging H₂ evolution rate of approximately 720 μmol/hr and 180 μmol/hr, respectively, thus implying that with an appropriate calcinations temperature, TiO₂/CuO(B) could be a potential photocatalysts under the renewable solar irradiation.

Figure 7.9 Comparison of H₂ evolution rate between UV-vis light and visible light over TiO₂/CuO(B)-450 and TiO₂/CuO(B)-750

The relatively much lower H₂ generation rate under the visible light activation compared to that under the UV-vis light could be attributed to the reduced irradiation spectrum thus lowering the degree of activation and probability for

photogeneration of electrons and holes, especially when TiO_2/CuO composite nanofibers possessed an overall more intense absorbance in UV light region than that of visible light region as illustrated in Fig. 5.7. Similar H_2 generation trend under UV-vis light and visible light was also reported by Maeda et al. (2011) (Maeda, Ohno et al. 2011). Besides showing that both CuO and Cu_2O could function efficiently in the TiO_2/CuO heterojunctions as the co-catalysts for H_2 generation under both UV-vis and visible lights irradiation, the importance of physicochemical properties synergy was again highlighted since $\text{TiO}_2/\text{CuO(B)}\text{-450}$ exhibited higher H_2 generation than $\text{TiO}_2/\text{CuO(B)}\text{-750}$ even under the activation of merely the visible light.

In addition to H_2 generation, concurrent TOC removal was observed to determine how the physicochemical properties influence the photocatalytic oxidation reaction which occurs in tandem with the photocatalytic H_2 generation. The overall TOC removal trend (Fig. 7.10) shows that the best physicochemical properties synergy for H_2 generation was also true for the photocatalytic oxidation of the methanol.

Figure 7.10 Dependence of TOC removal (%) on the calcinations temperature in photocatalysts under UV-visible light

As shown in Fig. 7.10, the highest TOC removal at the end of the 4- hours reaction was also observed over $\text{TiO}_2/\text{CuO(B)}\text{-450}$, approximated to be 12 %. This non-detrimental effect is favourable as methanol degradation involves the consumption

of photogenerated holes which helps prevent recombination of photogenerated electrons and holes thus increasing the availability of photogenerated electrons for H₂ generation. While adsorption thus specific surface area has been pointed out as the essential property in driving the photocatalytic oxidation of organic compound (Kudo and Miseki 2009), the lower TOC removal over TiO₂/CuO(B)-550 compared to that over TiO₂/CuO(B)-450 despite both having relatively higher specific surface areas has further implied that the larger crystal size of TiO₂/CuO(B)-550 could exert some negative effect on the overall photocatalytic efficiency. TiO₂/CuO(B)-350 has obviously lost its photocatalytic oxidation efficiency to the absence of mesoporosity as well as the low degree of crystallinity. However, endowed with a higher specific surface area which facilitated adsorption and mass transfer, TiO₂/CuO(B)-350 exhibited a relatively similar TOC removal as TiO₂/CuO(B)-650. Even though the good crystallinity possessed by both TiO₂/CuO(B)-650 and TiO₂/CuO(B)-750 could enhance the separation of photogenerated electrons and holes, the relatively similar TOC removal between TiO₂/CuO(B)-350, TiO₂/CuO(B)-650 and TiO₂/CuO(B)-750 as shown in Fig. 7.10 has implied that the negative effects from the much reduced specific surface area and lost of mesoporosity were more dominant. In brief, the overall TOC removal observation has further reinforced the proposed significance of physicochemical properties synergy on the photocatalytic efficiency of TiO₂/CuO(B).

Leachability of Ti and Cu from TiO₂/CuO(B) at different calcinations temperature was summarized in Table 7.3.

Table 7.3 Summary of leachability of Ti and Cu from photocatalysts

Photocatalysts	Ti (mg/L)			Cu (mg/L)		
	pH 2	pH 12	5%v/v glycerol	pH 2	pH 12	5%v/v glycerol
TiO ₂ /CuO(B)-450	0.386	0.880	0.008	16.75	0.089	0.836
TiO ₂ /CuO(B)-550	0.193	0.804	0.585	15.56	0.100	0.585
TiO ₂ /CuO(B)-650	0.195	0.528	0.000	11.15	0.037	0.224
TiO ₂ /CuO(B)-750	0.204	0.611	0.000	10.77	0.024	0.258

Lower Ti and Cu leaching were observed at higher calcinations temperature, possibly attributed to the good crystal growth rendering minimum defects within the overall crystal structure (Figs. 7.3, Fig. 7.4 and Table 7.1) which resulted in a stronger Ti and Cu affixation within the nanofiber. With this, synthesis of $\text{TiO}_2/\text{CuO(B)}$ could be customized and optimized to suit reaction solution pH as well as the objective of photocatalytic treatment.

7.4 Summary

By varying the calcinations temperatures, physicochemical properties such as the surface morphology, porosity, specific surface area, crystalline phase transformation, degree of crystallinity, crystal size and the elemental valence state, were observed to be interdependent and have jointly affected the photocatalytic H_2 and clean water generation efficiency of the as-synthesized photocatalysts. In this study, TiO_2/CuO composite nanofibers with 6 % mol Cu and calcined at 450 °C for 45 min ($\text{TiO}_2/\text{CuO(B)}$ -450) was found to be the best photocatalyst for H_2 generation without compromising the simultaneous TOC removal ascribing to the apt synergy of mesoporosity, specific surface area, well-dispersed and closely-contacted TiO_2/CuO heterojunctions for efficient charge separation, enhanced photoresponse into the visible light range, suitable crystallinity and crystal size. Higher calcinations temperature yielded lower Ti and Cu leaching, thus implying the feasibility to customize the synthesis of $\text{TiO}_2/\text{CuO(B)}$ to suit the pH of a reaction medium and expectation from a photocatalytic treatment. This study also implied energy saving opportunity since a low calcinations temperature was sufficient to yield efficient $\text{TiO}_2/\text{CuO(B)}$.

CHAPTER 8 CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion

8.1.1 Electrospun 1D TiO₂ nanofibers for H₂ and clean water generation from Cu-EDTA

For the first time, H₂, clean water, and reclaimed TiO/CuO composite nanofibers (TiO₂/CuO(A)) were harvested simultaneously through the photocatalytic treatment of Cu-EDTA. An excellent synergy was rendered by extending PCO and PCR of Cu-EDTA coupled with 1D electrospun TiO₂ nanofibers of superior physicochemical properties, thus resulting in a more efficient photocatalytic H₂ and clean water generation outcome. A comprehensive mechanism which clarifies the processes in this experiment was postulated for the first time, bridging the research gap. This approach (Approach A) has been initiated on the prime objective to adopt green chemistry to extend the viability of photocatalysis using TiO₂ to generate H₂ and clean water from waste water. This has been successfully demonstrated via: (1) elimination of prior complex synthesis process to modify and enhance TiO₂, (2) elimination of sacrificial reagent to enhance reaction efficiency for clean water and clean energy production, and (3) elimination of additional chemical to recover Cu. TiO₂/CuO(A) interestingly represents a novel potential photocatalyst for environmental remediation, implying the adoptability of Approach A to not only generate H₂ and clean water, but also to synthesize composite nanofibers from other organometallic wastewater in a green manner for wide applications.

8.1.2 Electrospun TiO₂/CuO composite nanofibers for H₂ and clean water generation

Approach B was subsequently attempted to produce composite nanofibers via electrospinning without compromising physicochemical properties, overcoming the limitation of reduced specific surface area posed by TiO₂/CuO(A) earlier. Emphasis was put on molecular mixing of Ti and Cu precursor while preserving the

simplicity of electrospinning and the entire synthesis process. For the first time, TiO₂/CuO composite nanofibers (TiO₂/CuO(B)) possessing novel integration of enhanced beneficial physicochemical properties were fabricated. Table 8.1 summarizes the characteristics of TiO₂/CuO(A) and TiO₂/CuO(B).

Table 8.1 Summary of characteristics of TiO₂/CuO(A) and TiO₂/CuO(B)

TiO ₂ /CuO(A)	TiO ₂ /CuO(B)
1. Sustained mesoporosity (of TiO ₂ nanofibers), but reduced specific surface area	1. Enhanced mesoporosity and specific surface area
2. High aspect-ratio	2. High aspect-ratio
3. Well-dispersed CuO for enhanced contact between TiO ₂ and CuO	3. Well-dispersed CuO for enhanced contact between TiO ₂ and CuO
4. Enhanced light absorption ability (red-shifted)	4. Enhanced light absorption ability (red-shifted)
5. Lower recombination of photogenerated charges	5. Lower recombination of photogenerated charges
	6. Smaller anatase TiO ₂ crystal size promoted by the Cu loading which renders higher contact area with TiO ₂ as well as shorter migration distance for photogenerated charge transfer to the surface reaction sites

Both TiO₂/CuO(A) and TiO₂/CuO(B) exhibited significant potential to concurrently evolve H₂ and degrade common organic pollutants such as AO7 and glycerol. Both photocatalysts were shown to be able to exploit the renewable solar energy to harvest H₂ and clean water from waste water. The demonstrated reusability and stability marked a great improvement from our previously developed CuO-incorporated TiO₂ nanoparticles and nanotubes which also lacked demonstration

and study on their reusability. It showed the significance of the novel approaches presented in this study for being facile and environmental friendly without compromising the photocatalytic efficiency of the composite through the synergy and stability of beneficial physicochemical properties. $\text{TiO}_2/\text{CuO(B)}$ showed a relatively more superior chemical stability thus lower leaching of its elements owing to $\text{TiO}_2/\text{CuO(B)}$'s synthesis nature which has endowed it with chemically stronger $\text{TiO}_2/\text{CuO}_2$ heterojunctions as well as its optimized Cu content. Overall, both approaches are promising in their own way for achieving environmental sustainability, depending on resource or material availability, application context and objective of TiO_2 photocatalysis.

8.1.3 Further study and optimization

The fundamental in-sight on how the main physicochemical properties affected the photocatalytic H_2 and clean water generation efficiency of TiO_2/CuO composite, was revealed. Good crystallinity was shown to enhance H_2 generation while high specific surface area enhanced photocatalytic oxidation of organic pollutant. Nonetheless, a good integration among physicochemical properties such as surface morphology, porosity, specific surface area, crystalline phase transformation, degree of crystallinity, crystal size and the elemental valence state, determined the overall synergistic effect on the final photocatalytic efficiency of $\text{TiO}_2/\text{CuO(B)}$. Through this initiative, the optimum Cu content that facilitated the best photocatalytic H_2 generation over $\text{TiO}_2/\text{CuO(B)}$ was determined to be 6 % mol ($\text{TiO}_2/\text{CuO(B)}-6$). The synthesis of $\text{TiO}_2/\text{CuO(B)}$ could be customized to suit an operational pH range of a reaction medium. Vivid changes of physicochemical properties were witnessed under the influence of different calcinations temperatures on top of their importance and synergy in governing the advantage of $\text{TiO}_2/\text{CuO(B)}$ and has provided a good fundamental for research advancement using electrospun $\text{TiO}_2/\text{CuO(B)}$ to generate clean energy and reclaim used water.

8.2 Recommendations for future study

Both novel approaches and composites in this study have demonstrated encouraging results thus paving opportunities and motivation for future research in environmental sustainability via TiO_2 photocatalysis, in particular for concurrent H_2 generation and organic pollutant decomposition. Each approach demonstrated its own uniqueness and suitability depends on one's treatment objectives and resource availability and accessibility. Overall, both approaches and composites represent a significant achievement in the field of TiO_2 photocatalysis in particular environmental sustainability. More future work will be beneficial to discover and build up on the empirical data to justify more fundamental theories. This is crucial to foster a deep understanding and firm foundation which will shed light for research strategies for $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ functional enhancement and practical application in future. The proposed experimental tasks are as follows:

8.2.1 Synthesis

Approach A remains an intriguing route for green synthesis of TiO_2/CuO composite with ample room for research and development. Like Approach B, a comprehensive and systematic investigation on the effect of Cu-EDTA waste water concentration on the physicochemical properties of TiO_2 nanofibers and the final composite could be undertaken to understand the effect on the final efficiency of $\text{TiO}_2/\text{CuO(A)}$, following which optimization could be carried out for different application. The concentration range of Cu-EDTA waste water feasible for Approach A could be further explored. Lower concentration of Cu-EDTA may yield a more efficient $\text{TiO}_2/\text{CuO(A)}$ as there would be lower Cu deposition and aggregation expected, thus a better light absorption ability and lower recombination rate between photogenerated charges. Nanocrystals size estimation via Scherrer equation should be carried out to further understand and address the effect of Cu loading and aggregation. Similar to $\text{TiO}_2/\text{CuO(B)}$, optimization could include chemical and physical stabilization of $\text{TiO}_2/\text{CuO(A)}$ via different heat treatment temperature and minimization or elimination of leaching.

Approach A could be extended to fabricating other TiO_2 -based composite nanofibers using other organometallic waste water; complete with the application spectrum of the reclaimed photocatalysts. This will enhance Approach A's potential as a platform for resource recovery from industrial waste water in the future.

Different electrospinning operating condition such as viscosity and flowrate of precursor solution, diameter of needle, as well as different voltage/distance setting could be pursued for both Approach A and B to gain more in-sights on the synthesis mechanism or process, as well as to determine more optimization opportunities.

The in-sights of the effect of other contaminants in the real wastewater are crucial, and should be investigated as this approach advances positively in the future, if a more realistic progress relative to the technological readiness scale is desired. Hence, with regards to $\text{TiO}_2/\text{CuO(A)}$ synthesis and reclamation from Approach A, a real Cu-EDTA wastewater should be considered for further research. A complete characterization of the real Cu-EDTA wastewater content should first be carried out to identify typical composition of Cu-EDTA wastewater from different industries and waste generators. Subsequently, the effect of the common constituents and their respective intermediate by-products on the photocatalytic efficiency, photocatalysts poisoning as well as the physicochemical properties, reclaim-ability, reusability, and efficiency of the resulting $\text{TiO}_2/\text{CuO(A)}$, could be investigated. The investigation could be initiated in two phases: (1) Study the independent or individual effect of each constituent using synthetic Cu-EDTA wastewater which would contain one of the other common constituents, one at a time; and (2) Study the combined effect of all the common constituents using the real Cu-EDTA wastewater. Comprehensive physicochemical characterization of the resulting $\text{TiO}_2/\text{CuO(A)}$ should be analysed for all reaction condition; following which usability, reusability, and stability of the composites in different pollutant models could be carried out to build up on the empirical data and evidence to address the independent and combined effects of the constituents involved.

8.2.2 Fundamentals

Use of $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ could be extended to numerous other wastewater and application. This would lead to the finding of how different reactant nature, characteristics or properties would affect the efficiency of $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$. Different operating condition such as the pH, waste water concentration, and light source (UV-vis and visible) on photocatalytic H_2 and waste water treatment could be investigated to build on the fundamental data.

The pollutant adsorption mechanism and kinetics on $\text{TiO}_2/\text{CuO(A)}$ and $\text{TiO}_2/\text{CuO(B)}$ could be studied as a function of pH, pollutant concentration, and photocatalyst concentration to investigate the photocatalyst-pollutant physicochemical relationship during the reaction process.

8.2.3 Application

More study needs to be undertaken before practical application of both approaches and composites can be considered.

As mentioned in 8.2.1, it is essential to evaluate the effect on the overall photocatalytic reaction using real wastewater, in order to make a more realistic progress and further determine the research outlook of Approach A and B in terms of real field application in future. The outcome of using real Cu-EDTA should be investigated for Approach A, as discussed in 8.2.1. Meanwhile, $\text{TiO}_2/\text{CuO(A)}$ (if possible from real Cu-EDTA wastewater) and $\text{TiO}_2/\text{CuO(B)}$ should be tested for concurrent H_2 generation and TOC removal from real glycerol and dye wastewater (and even other real organic wastewater available from the industries). Typical experimental work should consists of a comprehensive physical and chemical characterization of the wastewater (pH, temperature, chemical constituents, concentration), followed by investigation of the independent and combined effect of the other contaminants which may be present in the real wastewater (as proposed in 8.2.1). Effects such as photocatalysts poisoning, overall photocatalytic efficiency, and physicochemical change should be studied. Furthermore, evaluation could also be extended to include variable effect of different contaminant concentration and their respective intermediate by-products, different pH, and different temperature of

the respective wastewater; where the use of synthetic wastewater may be inevitable in this case if a test condition is not a typical condition of a real wastewater. Nevertheless, the motivation will be to build some fundamental data to encourage feasibility study by industrial wastewater generators to innovate their internal production processes, equipment facilitation, engineering and manufacturing procedure which possibly lead to future cleaner production initiatives and reduction of waste or degree of contamination.

Meanwhile, design of the experimental setup such as reactor, needs to be explored and diversified to identify possible setup variation, efficiency and feasibility in the real industrial context. Different reactor size and shape, flow types (batch, plug or continuous), as well as incorporation of instrumentation and control at a bench scale, could be evaluated prior to determining a considerable setup for advancement into the next experimental scale (i.e. pilot plant testing). Moreover, this could include innovation of potential technology to incorporate the composite photocatalysts such as membrane technology and pressure vessel; which may form another niche research area. In addition, set up could include provision for evaluation of photocatalysts' potential to harvest actual renewable solar energy into H₂ fuel and clean water. This would enable a more realistic quantification of actual solar irradiation and respective photo-absorption and photocatalytic efficiency.

Scaling up of synthesis via electrospinning is also crucial to estimate production cost and economics for real field application. For a start, industrial-scale components or equipment available for electrospinning could be sourced and attempted to fabricate the composite nanofibers. This may include determination of the usability, throughput, consistency, production capacity and functionality of the synthesized nanofibers. Further optimization of the precursor solution such as type of chemicals, solvents, concentration, volume, temperature, and viscosity; as well as equipment/parts engineering (for example the spinneret) or setup innovation may be among the required work in search for opportunity to enhance usability of equipment to synthesize the nanofibers of desirable properties with good consistency, production capacity and efficiency.

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