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Endorsed by	cal Kait
Ø	2 Chong Foes Debat
Signatifice of	Supervisor Alter
Bsuda Bsuda	Daini Brazinaco
Assoc. Prof.	Dr. Chong Fai Kait
Date :1	May 2011

UNIVERSITI TEKNOLOGI PETRONAS

DISSERTATION TITTLE: DEVELOPMENT OF Cu-Ni/TiO2 BIMETALLIC

CATALYST FOR PHOTOHYDROGEN PRODUCTION UNDER VISIBLE LIGHT

ILLUMINATION

by

ELA NURLAELA

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance this thesis for the fulfillment of the requirements for the degree stated.

Signature:

Main Supervisor:

Signature:

Co-Supervisor:

Signature:

Head of Department:

Date:

Assoc. Prof. Dr. Chong Fai Kait Fondamemal and Applied Sciences Department Universiti Tekaologi PETRONAS Bander Seri Iskandar, 31750 Tronoh Perak Darul Ridzuan, MALAYSIA Assoc. Prof. Dr. Chong Fai Kait
AP. Br. Mehomati Azavi Bustam@Khalil Asaga-Prolessor Chemical in recording Programme Chemical in recording Programme
Assoc. Prof. Dr. Mohd Azmi B Bustam@Khalil

Assoc. Prof. Dr. Shuhaimi B Mahadzir

18/5/2011

Dr. Shuhaimi Mahadzir Associate Professor & Head Chemical Engineering Department Universiti Teknologi PETRONAS

DEVELOPMENT OF Cu-Ni/TiO₂ BIMETALLIC CATALYST FOR PHOTOHYDROGEN PRODUCTION UNDER VISIBLE LIGHT ILLUMINATION

by

.

ELA NURLAELA

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BANDAR SERI ISKANDAR,

PERAK

MAY 2011

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DECLARATION OF THESIS

Title of thesis

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DEVELOPMENT OF Cu-Ni/TiO₂ BIMETALLIC CATALYST FOR PHOTOHYDROGEN PRODUCTION UNDER VISIBLE LIGHT ILLUMINATION

ELA NURLAELA

hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Witnessed by

(MAN

Signature of Author

Permanent address:

Jl. Tenjojaya 922, Cibadak, Sukabumi

Jawa Barat, Indonesia

Date: 18 May 201

Assoc. Prof. Dr. Chong Fai Kait Pendamensil and Applied Sciences Department University Teknologi PETRONAS Banger Seri Iskandar, 31750-Tronoh Perek Darul Ridzuan, MALAYSIA Signature of Supervisor

Assoc. Prof. Dr. Chong Fai Kait

Date : 18 May 2011

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ABSTRACT

Photocatalytic hydrogen production from water using TiO₂ as photocatalyst is one of the most promising method to produce hydrogen due to its low cost and environmental friendly process. However, it lacks the efficiency which is required in order to be economically feasible. This study is focused on enhancing the activity of TiO₂ to utilize visible light by Cu-Ni incorporation onto its surface, and also improving the overall photocatalytic hydrogen production by the addition of sacrificial agent. The incorporation of Cu-Ni onto TiO₂ was achieved by employing precipitation method and parameters such as calcination temperature and duration, Cu:Ni mass composition, and total metal loading were studied. The physical and chemical properties of the modified photocatalysts were investigated using Thermogravimetric Analysis (TGA), Fourier-Transformed Infrared Spectroscopy (FTIR), Field-emission Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (FESEM-EDX), Diffuse Reflectance UV-Vis Spectroscopy (DRUV-Vis), Surface area and porosity analysis, Temperature-programmed Reduction (TPR), and powder X-ray Diffraction (XRD). Morphology of the photocatalyst particle was spherical with slight agglomeration and high metal dispersion was achieved which was confirmed by XRD and FESEM-EDX analyses. It is believed that monometallic Cu/TiO₂ and Ni/TiO₂, and bimetallic Cu-Ni/TiO₂, were in their oxide form. The presence of Cu-Ni mixed oxide was detected by TPR analysis although it was not confirmed by XRD analysis due to the high metal dispersion. DRUV-Vis characterization showed that incorporation of Cu, Ni, and Cu-Ni onto TiO₂ shifted the absorption edge into visible region thus reducing the bandgap energy. The surface area of photocatalysts was found to be increased higher than that of bare TiO₂. In addition, the Cu-Ni/TiO₂ photocatalysts were studied for photocatalytic hydrogen production under visible light illumination from two reaction media: distilled water (H_2O) , and mixture of distilled water and glycerol (H_2O+gly) .

The photocatalytic study revealed that incorporation of Cu-Ni greatly enhances the photocatalytic activity of TiO₂. The highest amount of hydrogen evolved was 6.1 mL, three times higher compared to that obtained using bare TiO₂. $10wt\%_9Cu1Ni_200_1$, 10wt% metal loading photocatalyst with 9:1 of Cu:Ni mass composition, calcined at 200 °C for 1 h, was found as the best photocatalyst. The addition of glycerol (H₂O+gly) as sacrificial agent increased the amount of hydrogen evolved almost 1.5 times higher compared to that in (H₂O). The value added product as intermediates of glycerol oxidation such as glyceraldehyde, glycolic acid, and oxalic acid were also detected. The kinetics study also showed that the addition of glycerol addition enhanced the rate of photocatalytic reaction. The values of apparent rate constant (k) for photocatalytic hydrogen production from (H₂O) and from mixture of (H₂O+gly) were 0.3195 g^{0.84} L^{0.16} min⁻¹ and 0.3989 g^{0.805} L^{0.195} min⁻¹, respectively. On the other hand, the reaction order (n) with respect to photocatalyst amount were 0.160 and 0.195, for photocatalytic hydrogen production from distilled water (H₂O) and from mixture of water and glycerol (H₂O+gly), respectively.

ABSTRAK

Penghasilan hidrogen daripada air menggunakan pemangkinfoto TiO₂, merupakan kaedah yang paling sesuai bagi menghasilkan hidrogen kerana kos yang rendah serta mesra alam . Walaubagaimanapun, kecekapan yang kurang merupakan satu masalah untuk aplikasi yang praktikal dari aspek ekonomi. Fokus kajian ini adalah untuk meningkatkan aktiviti TiO₂ untuk penyerapan cahaya tampak yang optimum melalui penambahan Cu-Ni ke atas permukaan TiO2. Penggabungan TiO2 telah dicapai melalui kaedah pemendakan dan parameter kajian seperti suhu dan tempoh kalsinasi, komposisi jisim untuk Cu:Ni dan jumlah muatan logam. Penambahan agen pengorban juga dikaji untuk memperbaiki proses pemangkinfoto bagi penghasilan hidrogen. Sifat fizik dan kimia pemangkinfoto yang diubah, telah diuji menggunakan analisa termogravimatrik (TGA), Spektroskopi Inframerah Transformasi Fourier (FTIR), Mikroskopi Pengimbasan Elektron Pemancaran-Medan-Tenaga Penjerakan X-ray (FESEM-EDX), Spektroskopi Pantulan Tersebar UV-Vis (DRUV-Vis), analisa luas permukaan dan keporosan, Program Suhu untuk Penurunan (TPR) dan Pembelauan sinar-X bagi serbuk (XRD). Morfologi bagi pemangkinfoto adalah berbentuk sfera dengan sedikit agglomerasi dan penyebaran metal yang diperolehi adalah tinggi, seperti yang telah disahkan oleh analisis-analisis XRD dan FESEM-EDX. Dipercayai bahawa monologam Cu/TiO2, Ni/TiO2 dan juga dwilogam Cu-Ni/TiO2 wujud berada dalam bentuk oksida. Kehadiran oksida campuran Cu-Ni dapat dikesan dari analisis TPR walaupun ianya tidak dapat dikesan melalui analisis XRD disebabkan oleh penyebaran logam yang tinggi. Analisa sifat menggunakan DRUV-Vis menunjukkan bahawa penambahan Cu, Ni dan Cu-Ni kepada TiO₂ telah meningkatkan penyerapan spectra ke arah cahaya tampak, oleh yang demikian meningkatkan tenaga pemisahanband. Luas permukaan bagi pemangkinfoto ini telah meningkat berbanding dengan TiO₂.

Selain itu, penghasilan hidrogen menggunakan pemangkin-pemangkinfoto turut dijalankan dibawah illuminasi dampak didalam dua media: air suling (H₂O) serta campuran air suling dan gliserol (H₂O+gly). Pemangkinfoto terhasil daripada penambahan Cu-Ni meningatkan aktiviti pemangkinanfoto bagi TiO₂ dalam (H₂O) dengan banyaknya. Penghasilan hidrogen yang terbanyak adalah 6.1mL, tiga kali ganda lebih tinggi jika dibandingkan dengan penghasilan menggunakan TiO₂ sahaja. Pemangkinfoto dengan jumlah muatan logam 10wt% 9Cu1Ni 200 1, 10wt%, berkomposisi jisim Cu:Ni sebanyak 9:1, dikalsinasikan pada suhu 200 °C untuk 1 jam, merupakan pemangkinfoto yang terbaik. Penambahan gliserol (H2O+gly) sebagai agen pengorban meningkatkan amaun hidrogen yang terhasil, hampir 1.5 kali lebih tinggi jika dibandingkan dengan di dalam (H₂O). Produk penambahan-nilai sebagai perantaraan bagi pengoksidaan gliserol seperti gliseraldehid, asam glikolik dan asam osalik turut dikesan. Analisis kinetik juga menunjukkan kesan penambahan gliserol turut meningkatkan kadar tindakbalas pemangkinanfoto hidrogen. Nilai bagi pemalar kadar yang jelas (k) bagi penghasilan hidrogen secara pemangkinanfoto daripada (H2O)dan daripada (H2O+gly) adalah masing-masing adalah 0.3195 g^{0.84}L^{0.16}min⁻¹ and 0.3989 g^{0.805}L^{0.195}min⁻¹. Sebaliknya, tertib tindak balas (n) terhadap amaun pemangkinfoto untuk penghasilan hidrogen daripada (H₂O) dan (H₂O+gly) masingmasing adalah 0.160 and 0.195.

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LIST OF ABBREVIATIONS

CB Conduction band VB Valence band NHE Normal hydrogen electrode GC Gas cromatography HPLC High performance liquid croatography TGA Thermal gravimetric analysis FTIR Fourier-transformed infrared spectroscopy FESEM Field-emission scanning electron microscopy EDX Energy dispersive x-ray DR-UV-Vis Diffuse reflectance ultraviolet-visible BET Brunauer-Emmet-Teller BJH Barrett-Joyner-Halenda TPR Temperature-programmed reduction XRD X-ray diffraction Full width at half maximum FWHM

Visible light illumination

VLI

LIST OF SYMBOLS

e	Electron
h^+	Hole
E ^o (O ₂ /H ₂ O)	Electrochemical energy level of water oxidation, 1.23V vs NHE
E ^o (H₂O/H⁺)	Electrochemical energy level of water reduction, 0V vs NHE
W	Watt
R∞	Reflectance of the sample at infinite thickness
К	Absorption coefficient, Scherre's constant
S	Scattering coefficient
h	Planck's constant = $4.13566733 \times 10^{-15} \text{ eV.s}$
ν	Frequency of light
с	Speed of light = $2.99792458 \times 10^8 \text{ ms}^{-2}$
λ	Wavelength, nm
Eg	Bandgap energy, eV
k	Apparent rate constant, g/L/min
n	Order of reaction
r _o	Initial rate of reaction, g/min
θ	Diffraction angle of rays, °
Δm	Total weight loss, %
ω _A	Composition of anatase phase, %
ω _R	Composition of rutile phase, %
I _A	Maximum intensity of anatase phase, Cps
I _R	Maximum intensity of rutile phase, Cps

CHAPTER 1 INTRODUCTION

1.1 Hydrogen Production

The global energy demand has shown great escalation during the past decades. It is projected that world's primary energy demand will drastically increase by about 40% in 2030 of that in 2007 [1] which resultant increase fossil fuels utilization as energy sources. It is also predicted that by 2030 the demand of oil, coal, and natural gas, will increase approximately 24%, 54%, and 42%, respectively, compared to those in 2007. Although the energy resources may be sufficient to meet the enhanced demand, the environmental issue must be one of the main concerns for the future energy development. The excessive use of fossil fuels caused huge amount of emissions to the environment aggravating global warming [2]. Therefore, development of environmentally friendly energy resources is highly important for sustainable energy utilization in the future.

Hydrogen is one of the secondary energy resources that offers clean energy which can be produced from various feedstocks. The development of fuel cell energy based on hydrogen has attracted significant attention for years. However, the established hydrogen production routes utilize fossil fuel as feedstock which cause CO and CO₂ emission. Thus, clean hydrogen production remains a challenge. The hydrogen production technologies need to be reviewed so that it can overcome the sustainable energy and environmental concerns.

The current major routes of hydrogen production are based on fossil fuels which are non renewable resources and result in huge amount of emission.

It is reported that about 95% of the hydrogen production is derived from reforming natural gas, catalytic decomposition of natural gas, partial oxidation of heavy oils, coal gasification, and steam coal-iron gasification. A summary of various hydrogen production processes is shown in Table 1.1.

Primary	Process	Feedstock	Energy	Drawback
method				
	Steam reforming	Natural gas	Heat, possibly	70% efficient, will
			from nuclear	require carbon
			power plant	sequestration
	Thermochemical water	Water	High temperature	No emissions
	splitting		heat from	
			advanced gas-	
			cooled nuclear	
mal			reactor	
lher				
	Gasification	Coal	Steam and oxygen	Some emissions,
			at high temperature	will require carbon
		biomass	and pressure	sequestration
	Pyrolysis	Biomass	Moderately high	Some emissions,
			temperature steam	will require carbon
				sequestration
	Electrolysis	Water	Renewable,	Some emissions
[e]			including wind,	depending on
emic			solar, and	source of
och			electricity	electricity
lecti				
ы	Photoelectrochemical	Water	Direct sunlight	No emissions
	Photobiological	Water and alan	Direct suplicht	No emissions
Biological		straine	Ducer sumgur	
		strains		
	Anaerobic digestion	Biomass	High temperature	New, undeveloped
			steam	technology
	Fermentative	Biomass	High temperature	New, undeveloped
	microorganisms		steam	technology

Table 1.1 Summary of hydrogen production processes [3]

Among the processes, natural gas steam reforming is one of the most economical hydrogen production nowadays, because it is widely available, easy to handle, and has a high hydrogen-to-carbon ratio (H:C). Currently, around 80% of world hydrogen production use natural gas reforming process [4]. In this process, the catalytic cracking of natural gas (mostly methane) takes place in the presence of catalyst in high temperature steam creating hydrogen and carbon monoxide. Further, the unconverted methane and carbon monoxide is again reacted with steam in order to produce more hydrogen. Another process of hydrogen production that has reached maturity for commercial exploitation is coal gasification. Through this process, coal is converted into gaseous state by heating the coal in a reactor at very high temperatures. Further, the gaseous coal is treated with steam and oxygen and the result is the formation of hydrogen, carbon monoxide, and carbon dioxide. It is almost twice as expensive to produce hydrogen from coal compared to from natural gas due to the hydrogen-to-carbon ratio (H:C), which in natural gas is 4:1 and in coal is 0.8:1.8 [3]. However, this process produces a significant emission of carbon dioxide, SOx, and carbon monoxide. Hydrogen from water splitting through electrolysis has also been studied for large production. The process involves passing the electrical current through water between two electrodes, cathode and anode, to generate H₂ and O₂. This process generates relatively clean hydrogen with efficiency in the range of 80-90% [5]. However, electricity sources used for this reaction remains a problem since it still based on fossil fuel. In the thermochemical decomposition process water is split into H_2 and O_2 using a high temperature (below 1000 ^{0}C) in a cycle of thermochemical reaction [6]. Sulfur-iodine cycle, a Bunsen reaction involving iodine and thermal decomposition of iodine is one of the potential processes in thermochemical water splitting with overall efficiency about 50% [7]. Other cycle processes such UT-3 cycle, Browman-Westinghouse cycle and Zn/ZnO cycle are also being investigated and currently in the stage of the research and development [8].

Solar hydrogen production on the other hand has attracted much attention since it utilizes abundance resources for hydrogen production, sunlight as energy source and water as hydrogen feedstock. The process in which water is decomposed into H_2 and O_2 using solar energy as the driving force is a promising approach for clean and low-cost hydrogen production. It combines the advantageous hydrogen: properties of high

in energy content, environmentally friendly, ease of storage and distribution; and solar energy: in abundance, low risk and ecological acceptability. This process also might be a source of clean and abundant energy in a carbon-free natural cycle. When hydrogen is used as a fuel, water will be generated as the combustion product. The generated water could be recycled for photocatalytic hydrogen production using renewable primary energy (solar energy) [6]. However, the photocatalytic hydrogen production is facing a number of challenges in order to be economical feasible due to its low efficiency (below 10%). Therefore, further research and development efforts are necessary in order to enhance the efficiency of photocatalytic hydrogen production.

1.2 Photocatalysis and Photocatalyst

Photocatalysis is a term for the change of a chemical reaction rate or its initiation under the action of light radiation in the presence of a substance (the photocatalyst) that absorbs light and is involved in the chemical transformation of the reaction partners [9]. It involves the catalyst and light to bring out the chemical reaction [10]. Photocatalytic reaction is initiated when a photocatalyst is irradiated with photon energy higher or equal to its bandgap energy, an electron from the valence band jumped up to the conduction band, leaving a hole simultaneously in valence band. Such type of catalyst used in this reaction is called a photocatalyst. Some general properties that a photocatalyst need to posses: photocatalytically stable, biologically and chemically inert, cheap, and non-toxic [11].

Semiconductor is a common material used as photocatalyst due to its electronic structure of the metal atom during chemical combination. Semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band, and the lowest empty band, called conduction band. These two bands are separated by a bandgap. Herein, a bandgap can be defined as the difference of energy in these two bands [12]. Some semiconductors have been reported to meet the above-mentioned requirements. CdS, CdSe, TiO₂, ZnO, Fe₂O₃, ZnS, and WO₃ being typical examples.

In term of photocatalytic hydrogen production, TiO_2 is the most used photocatalyst compared to the others. Among the common photocatalysts, ZnO, Fe_2O_3 , and WO_3 have also been extensively investigated. However, ZnO is easily photo-corroded under irradiation by photogenerated holes and unstable in illuminated aqueous solutions, especially at low pH values. WO₃ on the hand are stable photocatalysts for O₂ evolution under visible light irradiation, but no H₂ is evolved due to their low conduction band. Their conduction bands are located at a more positive potential than potential for water reduction [11]. Other metal chalcogenide photocatalysts such as CdS and CdSe meet the requirement as low bandgap photocatalysts. However, they are not stable in photocatalytic water splitting due to the presence of S²⁻ and Se²⁻ anions. These anions caused the CdS or CdSe itself to be degraded and oxidized because they are more suspectible to oxidation than water [11]. Figure 1.1 displayed the photocatalysts and their bandgap position.





Certain photocatalysts such as $SrTiO_3$, TiO_2 and $NaTaO_3$ have been extensively investigated for photocatalytic hydrogen production since they show good photostability and non-photocorrosive under light irradiation. However, their large bandgap energy remains a problem in order to achieve the efficient photocatalytic hydrogen production. Lower bandgap energy is essential for photocatalytic hydrogen production so it can be performed under visible light illumination. As the solar radiation has only 4-5% of UV-light [13], it is crucial to develop a photocatalyst with better visible light absorption. The schematic diagram of light spectrum is presented in Figure 1.2.



Figure 1.2 Electromagnetic spectra [14]

Studies on photocatalytic hydrogen production over TiO_2 have clearly revealed that high bandgap energy is one of the main problems to gain high efficiency. The bandgap of TiO_2 is about 3.2 eV which makes it unable to utilize visible light. Another phenomenon which gives detrimental effect on photocatalytic hydrogen production is recombination reaction between photogenerated holes and electrons. The photogenerated holes and electrons react in a very short period (in term of nanosecond) which reduce the opportunity of electrons to react with water and reduced it to form H₂.

Numerous studies have been reported to improve the efficiency of photocatalytic hydrogen production by modifying all the systems that involve in this reaction as will be reviewed in Chapter 2. Bimetallic photocatalysts have shown remarkable promise. In the above context, objectives of the present study are:

 To develop bimetallic Cu-Ni/TiO₂ photocatalyst by optimizing some factors such as calcination temperature and duration, Cu:Ni mass ratio, and total metal loading

- 2. To study the effect of sacrificial agent (glycerol) addition on photocatalytic hydrogen production
- 3. To determine the value-added products from glycerol oxidation
- 4. To study the kinetic of photocatalytic hydrogen production.

2.1 Scope of Study

In this study, modification of TiO₂ with incorporation of Cu and Ni was applied. Cu and Ni were incorporated onto the surface of TiO₂ in the form of CuO and NiO. The chemical and physical properties of photocatalyst such as surface area, crystal size, and surface morphology were investigated by means of Thermogravimetric Analysis (TGA), Fourier-Transformed Infrared Spectroscopy (FTIR), Field-emission Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (FESEM-EDX), Diffuse Reflectance UV-Vis Spectroscopy (DRUV-Vis), Surface area and porosity analysis, Temperature-programmed Reduction (TPR), and powder X-ray Diffraction (XRD).

In order to optimize the performance of bimetallic photocatalyst, some factors which affect its physical and chemical properties such as calcination temperature and duration, Cu:Ni ratio, and total metal loading was also investigated. Addition of glycerol as sacrificial agent to increase the photocatalytic hydrogen production was perfomed and its oxidation products was investigated.

CHAPTER 2 LITERATURE REVIEW

2.2 Titanium Dioxide Photocatalysis

Titanium dioxide or titania, TiO_2 , is the most well-known researched photocatalyst for various photocatalytic reactions due to its excellent chemical and electrical properties [15]. It exists naturally in the form of anatase, brookite, and rutile. Among these structures, anatase and rutile are the most common types of TiO_2 crystal. In anatase and rutile structures, the basic building block consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the apices of octahedron are slightly longer [16].



Figure 2.1 Crystal structures of a) anatase, b) rutile, and c) brookite

Anatase is thermodynamically unstable with the transition to rutile at 700 °C [17]. However, due to its photoactivity, anatase is more widely used as photocatalyst [18]. It has bandgap energy of 3.2 eV corresponding to the ultraviolet light at 388 nm. On the other hand, rutile crystal, the most stable form of TiO_2 at normal temperature and pressure, has a bandgap energy value of 3.0 eV corresponds to the ultraviolet light at 400 nm [18].

Although rutile structure exhibits lower bandgap energy, its photoactivity is lower than that of anatase due to the position of the conduction band. The conduction band of anatase is closer to the negative position than in rutile; therefore, the reducing power of anatase is stronger than that of rutile [20].

The well-known commercial TiO₂-Degussa P25 contains both rutile (15%) and anatase (85%) structures and has been reported to be the active photocatalyst for various reactions. Kirchenerova *et al.* [21] reported that TiO₂ - Degussa P25 is more active for n-butanol photooxidation than that of Hombicat UV 100 resulting in 95% conversion.



Figure 2.2 Band structures of anatase and rutile [16]

The higher activity of TiO_2 - Degussa P25 was also reported by Zielinska *et al.* [22] on the study of photocatalytic degradation of reactive black 5 over TiO_2 -Tytanpol A11 and TiO_2 - Degussa P25.

It was reported that TiO_2 - Degussa P25 displayed 30% higher activity than that of TiO_2 -Tytanpol A11 in all cases (different operating conditions). Zielinska *et al.* [23] also reported in another work that TiO_2 Degussa P25 displayed higher activity compared to that of TiO_2 -Tytanpol A11 for photocatalytic degradation of two types of textile dyes, namely Acid Black 1 and Acid Blue 7.

Research by Bowering *et al.* [24] reported the photocatalytic degradation and reduction of nitric oxide over TiO_2 - Degussa P25. The enhancement of TiO_2 - Degussa P25 photoactivity is mainly due to its mixed composition which resulted in higher surface area, higher anatase crystallinity, and narrow pore size distribution [25].

2.3 Titanium Dioxide for Photocatalytic Hydrogen Production

Photocatalytic hydrogen production using TiO_2 has attracted much attention from researchers as the most promising method for clean, low-cost, and environmentally friendly solar hydrogen production. Due to the high chemical and photochemical stability, moderate bandgap, non-toxicity, and high surface area, TiO_2 is considered as a good photocatalyst. The moderate price of TiO_2 compared to other photocatalysts also becomes an advantage.

The basic mechanism of photocatalytic water splitting is displayed in Figure 2.2. The photocatalytic water splitting occurs when the photocatalyst absorbs photon with energy equal or greater than its bandgap energy and generates photoexcited electrons in the valence band. Subsequently, the electrons migrate to the conduction band and simultaneously leaving the holes in the valence band. The photogenerated electronsholes can recombine in the bulk or surface of photocatalyst within a very short period. When the recombination reaction is prevented, the photoexcited electrons and holes separate, migrating to the surface and finally, absorbed species are reduced and oxidized by photogenerated electrons and holes to produce H_2 and O_2 , respectively [26], [27].

In terms of photocatalytic hydrogen production, the conduction band level should be more negative than water reduction level $(E_{H_1/H_2O} = 0V vs NHE)$ while the valence band level should be more positive than water oxidation level $(E_{O_1/H_2O} = 1.23V vs NHE)$ [19]. For TiO₂ photocatalyst, the reaction is expressed as follows:

$$TiO_2 + 2h\nu \rightarrow e^- + h^+$$
 (2.1) [15]



Figure 2.3 Basic mechanism of photocatalytic water splitting [19]

The photogeneration and migration of electrons and holes are strongly dependent on the structural properties of photocatalyst while the oxidation and reduction by electrons and holes are promoted by the presence of a solid co-catalyst loaded onto the photocatalyst surface to produce active sites and for reduction in bandgap energy [28]. However, the use of bare TiO_2 as photocatalysts resulted in low efficiency (below 10%) which led to problem for economically feasible hydrogen production [29].

2.4 Modification of Titanium Dioxide

In order to overcome the low efficiency of photocatalytic hydrogen production, modification has been conducted on TiO_2 surface and the reaction system. The modification is aimed to develop TiO_2 photocatalyst with better properties for photocatalytic hydrogen production, which is affected by three factors, i.e.:

separation efficiency for the photogenerated electrons-holes; water reduction efficiency of photogenerated electrons, and visible light activity of the photocatalyst.

Some modification mentioned above include ion implantation, sensitization, transition metal doping, and metal doping to improve the photocatalytic activity of TiO_2 as well as addition of a sacrificial agent to the system to enhance the photocatalytic hydrogen generation.

2.3.1 Ion Implantation

Metal ion implantation has been widely used as the effective method to improve the photocatalytic activity of TiO_2 towards visible light region. Through this method, the electronic structure of TiO_2 was modified and its photoresponse shifted to the visible region. The process starts when the high-energy transitional metal ions are injected into the lattice of TiO_2 and interact with TiO_2 .

On the investigation of photocatalytic decomposition of NO, Takeuchi et al. [30] studied the use of TiO₂ thin film prepared using combination of ionized cluster beam (ICB) and advanced metal-ion-implantation method. In this method, TiO₂ thin film was prepared through heating the Ti metal up to 2200 K followed by introducing the Ti vapor into a high vacuum chamber to produce titanium clusters. In the vacuum chamber, the titanium clusters reacted with O₂ molecules to form TiO₂ thin film. Later, the TiO₂ thin film was implanted with Cr ion using ion implanter. For comparison, the chemically Cr-doped TiO₂ was also prepared by wet impregnation method. It was observed that the implanted Cr-TiO₂ thin film shifted the absorption spectrum into the visible region. On the other hand, Cr ions chemically doped on the surface of TiO₂ did not shift the absorption spectrum. As a result of formation of the impurity energy level within the bandgap of TiO₂, chemically doped Cr also exhibited the new absorption peak. Study on their photoactivity for NO decomposition revealed that under visible right irradiation, implanted Cr-TiO₂ thin film displayed the highest photoactivity. The highest activity at visible region might be due to the modified electronic structure of TiO₂ thin film as a result of its interaction with implanted Cr ions in the bulk side of the film. Herein, the Cr ions did not work as the recombination center but only to modify the electronic structures thus enhancing the ability to utilize visible light. On the other hand, no decomposition of NO was observed for undoped TiO_2 thin film and chemically doped TiO_2 .

Fe ion implanted in TiO₂ for photocatalytic degradation of 2-propanol was investigated by Yamashita *et al.* [31] and similar trend in performance was found with the work by [30]. Other metal implantation using V and Sn have been reported as an effective method to improve photocatalytic performance of TiO₂ toward visible light [32]-[35]. The substitution of octahedrally coordinated Ti⁴⁺ ion with metal ion in the lattice of TiO₂ causing the mixing of Ti(d) orbital of Ti oxides with metal(d) orbital of the implanted metal ion. Therefore, the bandgap of implanted metal-TiO₂ reduce and leads to the enhancement of visible light utilization.

Study on non metal-ion implantation was also investigated and reported in some papers [36], [37]. The effect of non metal ions such as N, F, S is explained by mixing of their derived p states and O 2p states that led to bandgap narrowing [20]. However, different result was found by Diwald *et al.* [38]. Investigation of the incorporation of N⁻ ion into TiO₂ crystal for photodeposition of oxygen was found to give detrimental effect. The effect is attributed to the partial filling of conduction band by electrons causing shift to energies higher than the bandgap.

2.3.2 Sensitization

2.3.2.1 Composite Semiconductor

Another method for improving the activity of photocatalyst toward visible region is by producing composite semiconductor. Through this method, a large-bandgap semiconductor is coupled with a small-bandgap semiconductor having more negative CB level. When semiconductors irradiated with visible light, the photogenerated electrons will be injected from the small-bandgap semiconductor to the large-bandgap semiconductor, while the holes will be injected from the large-bandgap semiconductor to the small-bandgap semiconductor. These processes increase the photogenerated charges transfer thus retarding the electrons-holes recombination. Further, the accumulated electrons at the CB large-bandgap semiconductor react with protons to produce H_2 [20], [26].

It has been reported that some small-bandgap semiconductors coupled with TiO₂ results in enhancing the visible light activity [39], [40]. So et al. [41] reported the synthesis of CdS/TiO₂ by co-hydrothermal process of CdS and TiO₂ and its activity was investigated for photocatalytic hydrogen production. In this study, the ratio of CdS and TiO₂ was varied and the physical properties of this photocatalyst were controlled by the surface treatment with TiCl₄ aqueous solution. Better interaction between TiO₂ and CdS was observed since the etching effect of TiCl₄ is believed to improve the photohydrogen production rate and its photocurrent. Keller and Garin [42] investigated the binary and ternary composite semiconductors, namely WO₃/TiO₂, SiC/TiO₂, and WO₃/SiC-TiO₂ for photocatalytic oxidation of methylethylketone in gas phase. Comparatively, the binary composite semiconductors SiC/TiO₂ displayed higher photocatalytic activity compared to those of binary WO_3/TiO_2 and bare $TiO_2.$ On the other hand, binary WO_3/TiO_2 displayed inferior performance when compared to that of bare TiO2 due to a surface poisoning. The composite semiconductor, WO₃/SiC-TiO₂, displayed the highest ternary photocatalytic activity as compared to other photocatalysts with conversion of MEK up to 80%. The presence of a second semiconductor, SiC, affects the photocatalytic activity by retarding the hole recombination reaction. In this system, electrons were transferred from the conduction band of SiC to the conduction band of TiO₂, while holes were transferred from the valence band of TiO₂ to the valence band of SiC. The simultaneous electrons-holes transfer increased the charge transfer separation thus retarding the electrons-holes recombination. WO3 on the other hand, involved in electron transfer in the conduction band of TiO2. It acted as the electron accepting species on the surface of TiO₂ which is effective to prevent electrons-holes recombination.

2.3.2.2 Dye Sensitization

Dye sensitization is widely used to improve the photocatalytic activity of TiO_2 toward visible region. Organic dye plays the same role as small-bandgap semiconductor in composite semiconductor as shown in Figure 2.3. In this system, under illumination, the photogenerated electrons from dye were transferred to the conduction band of TiO_2 to initiate water reduction. On the other hand, the holes in dye were reduced by sacrificial agent to regenerate the dye for the whole reaction. The electrons-holes recombination in dye itself occurred in a matter of nanosecond or microsecond, while the injection of electrons to semiconductor was in the order of femtosecond [19]. Therefore, in order to gain efficient electrons transfer from dye to semiconductor, the electrons injection process must occur in a very short period.

Some dyes have been reported to be efficient in photocatalytic hydrogen production under visible light illumination [43]-[46]. Hirano *et al.* [46] reported on the photocatalytic hydrogen production using Pt/TiO₂ sensitized by several types of dyes, namely Ru(bpy)₃²⁺, tris(bipirimidine)Ru(II) Ru(bpym)₃, and porphines, in the presence of EDTA as sacrificial agent. Tris(bipirimidine)Ru(II) Ru(bpym)₃ was found to be the most efficient dye to enhance the photocatalytic activity due to its higher affinity for TiO₂ surface. The effect of dyes concentration and Pt loading were also observed and the corresponding results showed that there was an optimal value. Additional Pt loading or dye content led to the reduction in photocatalytic hydrogen production rate.



Figure 2.4 Photocatalytic H₂ production with dye-sensitized TiO₂ [19]

2.3.3 Metal Doping

Metal doping has been reported as one of the effective methods to enhance photocatalytic hydrogen production. However, since so many factors affected the photoactivity of TiO₂ photocatalyst, the effect of metal doping, both detrimental and beneficial, have been reported. Method of metal doping, metal content, type of metal, and the experimental conditions are the main factors affecting the photoreactivity of doped photocatalyst [47], [48]. Metal deposition on TiO₂ can be achieved by applying some methods, i.e. co-precipitation [49], photodeposition [50], liquid impregnation [51], mechanical alloying [52], and sol-gel method [47], [53], [54]. On the surface of TiO₂, metal dopant can act as an electron and/or a hole trap which inhibits the electron-hole recombination reaction while providing active sites for reaction. Another effect from metal incorporation is reduction in bandgap energy which leads to shift in the absorption region of photocatalyst to visible range.

Noble metal doping including Pt, Au, Ag, and Pd has been intensively developed in order to enhance the ability to TiO_2 to utilize visible light [55]-[61]. The lower Fermi level of noble metals compared to that of TiO_2 led to efficient separation of photogenerated electrons and holes. The photogenerated electrons were quickly transferred to metal particles deposited on the surface of TiO_2 , while the photogenerated holes remain on TiO_2 [25]. As a result, reduction by the photogenerated electrons occurred on the metal particles while oxidation by the photogenerated holes occurred on TiO_2 [62].

Rosseler *et al.* [63] reported the comprehensive study of photocatalytic hydrogen production over a series of Pt/TiO₂ and Au/TiO₂ photocatalyts. Comparison study of different TiO₂ was conducted by varying the anatase/rutile content, based on sol-gel synthesis and commercial TiO₂. It was found that Pt- and Au-doping on both synthesized and commercial TiO₂ greatly enhanced the hydrogen production. However, the highest amount of hydrogen evolved was obtained with Au as cocatalyst; Pt co-catalyst was found to be less active. This might be caused by the reactivity of Pt. Pt is very active (more than Au) for the reverse reaction of H₂O splitting even at room temperature, decreasing the efficiency of photocatalytic hydrogen production. Au/TiO₂ was identified as the photocatalyst with the lowest bandgap energy thus extending the photoresponse of TiO₂ into the visible spectra. Other parameters such as crystallinity, surface area, the nature of metal deposited, metal content, and the anatase/rutile ratio were also reported as the factors that affect the effective photocatalytic hydrogen production.

Study on Ag doped TiO₂ was reported by Behnajady *et al.* [51] and Dobosz and Sobczynski [64]. By applying liquid impregnation and photodeposition, Ag was doped on the surface of TiO₂. Doping with Ag increased the photocatalytic activity of bare TiO₂ with the maximum activity achieved at 0.5 and 2 mol% for photodeposition and liquid impregnation method, respectively.

Generally, metal doping onto the surface of photocatalyst gave better effect in increasing the photocatalytic activity. However, in the study of TiO₂ doped with various metals i.e. Ag, Pd, Pt, Fe, Zn, and Zr [65], slight difference in results were found. Doping with Ag, Pt, and Pd resulted in higher photocatalytic activity while Fe, Zn and Zr doping had detrimental effect due to the greater crystal size and lower surface area. The lower electronegativity and lower electron affinity of metal dopant also become factors of inferior performance of metal-doped photocatalyst [48]. The lower electronegativity of metal dopant compared to that of Ti led to more difficult photoexcited electron transfer to the surface of photocatalyst. As a result, the metal

dopant becomes an electron-transfer inhibitor thus increasing the electrons-holes recombination. On the other hand, high electron affinity is necessary in order to maintain the electrons stability until the photogenerated holes were being reduced on the surface of photocatalyst.

In order to replace the use of expensive noble metals dopant (Pt and Au), investigation for low cost and easily available metal dopant is required. Researchers have attempted to develop transition metal doping on TiO₂. Di Paola et al. [66] developed transition metal (Fe, Cu, Co, Cr, V, W, Mo) doped TiO2 with incipient wetness impregnation method for ethanoic acid and 4-nitrophenol photooxidation. Among those transition metals, a beneficial influence of metal loading on TiO₂ was found only for Cu/TiO2 for ethanoic acid photooxidation while W/TiO2 for 4nitrophenol photooxidation. The more positive redox potential of Cu/Cu⁺ compared to the conduction band of TiO₂ caused the loaded Cu reduced into metallic state (Cu⁰) and acts as co-catalyst. This phenomenon might increase the photocatalytic activity of TiO₂ photocatalyst. On the other hand, Gao et al. [54] reported a different behaviour of Zr on TiO₂ for photocatalytic degradation of biphenol A. Doping with Zr improved the photocatalytic activity although the absorption of photocatalyst shifted to the shorter wavelength. The photocatalytic activity was enhanced as the result of bandgap enlargement. The conduction band shifted towards higher potential causing the stronger reduction of photogenerated electrons which is favorable for photocatalytic reaction.

Another work of transition metal doping on TiO_2 for photocatalytic hydrogen production was studied by Dholam *et al.* [67]. Cr and Fe were doped onto the TiO_2 film by applying radio- frequency magnetron sputtering and sol-gel method. Fe/TiO₂ showed better photocatalytic activity with higher amount of hydrogen evolved compared to that obtained with Cr/TiO₂. Better photoactivity of Fe/TiO₂ is connected to the shifting of the absorbance towards higher wavelength. Fe ion also acts as electrons and holes scavenger thus avoiding recombination reaction. On the other, although Cr/TiO₂ showed better absorption in visible range, Cr can only trap one type of charge carrier (electron) besides forming recombination sites that reduce the photocatalytic activity.
2.3.4 Bimetallic Photocatalysts

Supported bimetallic catalysts have been investigated and showed better performance for various reactions compared to that of monometallic [68]. The improvement of catalytic activity in bimetallic catalysts might be due to changes in the properties of the homogeneous alloy particles. These changes maybe due to the formation of active surface structures, surface enrichment of a particular metal or by a combination of all these effects [69]. In term of photocatalytic reaction, use of bimetallic photocatalyst is reported as one of the effective method to improve the efficiency of photocatalytic reaction due to the beneficial synergetic effect of two different metals [70], [71].

Wang *et al.* [70] investigated the photocatalytic activity of monometallic Fe/TiO₂, Bi/TiO₂, and Co/TiO₂ and bimetallic Fe-Co/TiO₂ and Bi-Co/TiO₂ for rhodamine photodegradation. It was found that the bimetallic Fe-Co/TiO₂ displayed the highest photoactivity, although higher absorbance at visible range was obtained for Fe/TiO₂ and Bi-Co/TiO₂. The highest photodegradation, about 65% was achieved with Fe:Co mole ratio of 1:5. The synergetic effect of two different dopants is believed to give better result for photodegradation of rhodamine. Herein, the Fe(III) ion acts as the hole trap while the Co(II) ion acts as the electron trap thus reducing the electron-hole recombination reaction. On the other hand, for Bi-Co/TiO₂, both Bi(III) and Co(II) act as electrons accumulation sites, which only improved the interfacial charge transfer.

As a result, $Bi-Co/TiO_2$ did not enhance the photocatalytic activity under visible light region shown by Fe-Co/TiO₂.

Recently, study on bimetallic photocatalyst for photocatalytic hydrogen production was investigated by Mizhukoshi *et al.* [71]. Bimetallic Au-Pd/TiO₂ was prepared using sonochemical method and its photocatalytic activity was studied for photohydrogen production from ethanol aqueous solution. Interestingly, compared to previous bimetallic photocatalyst described earlier, the Au-Pd/TiO₂ photocatalyst was prepared in the form of Au-core/Pd shell on the surface of TiO₂. For comparison, the monometallics Au/TiO₂ and Pd/TiO₂, and also the annealed bimetallic Au-Pd/TiO₂ alloy were also studied. The highest hydrogen production rate was obtained using 0.25Au-core/0.75Pd-shell. It was observed that on the surface of TiO₂, the Au-core becomes the electron accumulation sites to hinder the recombination of charge carrier. Electrons accumulation was not found both in Au/TiO₂ and Pd/TiO₂. In addition, the presence of thicker Pd shell shields the electrons from recombining with holes. Therefore, higher Pd content displayed superior performance on its photocatalytic activity. Comparing with annealed Au-Pd/TiO₂ alloy, under visible light illumination, Au-core/Pd shell on the surface of TiO₂ showed better performance. However, under UV-light illumination, annealed Au-Pd/TiO₂ alloy displayed higher photocatalytic activity than that of Au-core/Pd shell on the surface of TiO₂.

As described in Section 2.3.3., Pt and Au loading were the most effective method for improving the photocatalytic activity. However, taking into account the economical aspect of photocatalytic hydrogen production, it is necessary to consider the low cost metal to replace the use of Pt and Au. A comparative study on noble metal (Au and Pd) loading with Cu loading reported by Sreethawong and Yoshikawa [72] proved that Cu loading onto the surface of TiO_2 is comparable for photocatalytic hydrogen production. The optimum loading of Cu, Pd and Au were 1.5, 1.2, and 2 wt%, respectively, and the amount of hydrogen evolved for these loadings were 360, 420, and 557 µmol.h⁻¹, respectively. Another work from Puangpetch et al. [48] investigated the effect of metal type and loading on SrTiO₃ photocatalyst for photocatalytic hydrogen production. By applying sol-gel method, several metals (Au, Pt, Ag, Ni, Ce, and Fe) were incorporated onto the surface of SrTiO₃ photocatalyst. The results clearly revealed that incorporation of Ni gave advantageous effect as similar to Au-, Pt- and Ag-doping although the amount of hydrogen evolved is still lower than those obtained from noble metal-doped photocatalysts. However, compared to Ce and Fe doping, Ni doping gives beneficial effect by enhancing the hydrogen production rate.

2.3.5 Cu- and Ni-Doped Photocatalysts

Intensive study on incorporation of copper and nickel in order to enhance the activity of TiO_2 has been reported in numerous papers [52], [73]-[77]. Colon *et al.* [47] investigated the improvement of TiO_2 performance with Cu dopant. The Cu/TiO₂ was prepared by sol-gel method and its activity was studied for photocatalytic oxidation of phenol.

It was found that doping with Cu increased the surface area of photocatalyst, enhancing the absorption into the visible range, thus resulted in higher quantum yield of phenol oxidation. Doping with Cu is believed to accelerate the process of electrons transfer to oxygen as the rate limiting step in this reaction. On the other hand, according to Choi and Kang [78], doping Cu onto the surface of TiO₂ did not affect the absorption of TiO₂, which was indicated by the same pattern of absorption spectra for bare TiO₂ and Cu/TiO₂. It was also found that in this case, Cu was incorporated on the external surface of TiO₂ in the form of CuO. On the external surface of TiO₂, CuO will be reduced into Cu or Cu₂O by attracting the photogenerated electrons from TiO₂ valence band. The reduction of CuO thus hindered the electrons-holes recombination and increased the photocatalytic reaction. However, Cu doping on TiO₂ may provide both beneficial and detrimental effects as reported by Wu and Lee [79]. They found that deposition of Cu particles greatly enhance the photocatalytic hydrogen production from water-methanol mixture. On the other hand, when Cu was doped in the lattice of TiO₂, the overall photocatalytic reaction was found to decrease.

Cu-doping was also employed for composite photocatalyst as studied by Miwa *et al.* [73]. Different photocatalyst, namely ZnO/TiO₂, SnO/ TiO₂, CuO/ TiO₂, Al₂O₃/TiO₂, and CuO/Al₂O₃/TiO₂ were studied on photocatalytic hydrogen production from aqueous methanol solution. Among these photocatalysts, the highest photocatalytic activity was obtained using CuO/Al₂O₃/TiO₂. The doping concentration of CuO and Al₂O₃ has a correlation on photocatalytic hydrogen production. The optimum CuO loading was 0.2 wt% when Al₂O₃ loading was 0.3 wt%. However, as the Al₂O₃ loading increased, the optimum loading of CuO tend to be decreased. The highest amount of hydrogen evolved was obtained with 0.2 wt% CuO/0.3 wt% Al₂O₃/TiO₂. The synergetic effect of composite photocatalyst is the main factor in the improvement of TiO₂ photocatalytic activity. However, in this study, the synergetic effect itself was not clearly revealed. This might be as a result of charge transfer power interaction and an adsorption activity of the reactants for the co-catalyst CuO and Al₂O₃.

Nickel on the other hand, has been found to be one of the effective transition metal dopant to improve the photocatalytic activity of some semiconductors for photocatalytic hydrogen production [80]-[84]. In the study of Ni doping on InTaO4, Chiou *et al.* [82] analyzed that Ni existed in the form of NiO. Hence, NiO affected the photocatalytic activity by shifting the absorption spectra to the visible range. The absorption spectra extended to longer wavelength (680 nm). The number of active sites was found to increase when Ni was loaded onto the photocatalyst. The maximum amount of hydrogen evolved was 14.9 μ mol.g⁻¹ on 3wt% NiO_x/InTiO₄, about 10 times higher compared to that obtained without NiO doping. However, after a certain time, deactivation of photocatalyst was found when NiO dissolved in the aqueous solution and formed Ni(OH)₂.

Ni metal doping was also employed on the TiO_2 thin film using magnetic sputtering technique [85]. It was observed that Ni dopant greatly enhances the photocatalytic activity of TiO_2 by shifting the absorption spectra, changing the phase composition and providing more active sites.

Another study of Ni doped TiO₂ was reported by Jing *et al.* [80]. Ni/TiO₂ was prepared by sol-gel method and its activity was studied for photocatalytic hydrogen production in aqueous methanol solution under UV-Vis light illumination. The presence of Ni led to a higher surface area and narrower pore size distribution which affect the photocatalytic activity of TiO₂. The highest amount of hydrogen evolved was found for Ni doping of 1wt% (185 μ mol.h⁻¹), further increased on Ni doping led to the decrease of hydrogen production rate due to the blocking of the photocatalyst active sites. They also revealed that in this case, Ni acts as holes trap, considering that Ni²⁺ position is near the valence band of TiO₂. On the surface of TiO₂, Ni²⁺ trapped a hole and will be oxidized to Ni³⁺. Then, Ni³⁺ quickly reduced to Ni²⁺ due to its instability.

A slight difference with Cu doping as described earlier, Ni incorporation into the crystal structure of TiO_2 results in narrowing the bandgap thus led to better performance of the photocatalyst [86]. In this study, the photocatalyst co-doped with Ni and N was prepared by sol-gel method.

For comparison studies, N/TiO₂ and Ni/TiO₂ were also prepared and studied for photocatalytic degradation of formaldehyde. Interestingly, the activity of Ni/TiO₂ was lower than that of N/TiO₂ and bare TiO₂. However, when compared to N-Ni/TiO₂, N/TiO₂ was found to be less active. The result indicates that Ni incorporation could enhance the photocatalytic activity of TiO₂. Ni existed in the form of Ni₂O₃ and dispersed on the surface of TiO₂, lowering its bandgap energy and reducing the photogenerated electrons-holes recombination.

Use of Cu and Ni for bimetallic catalyst has been reported as the effective method to improve the efficiency of various reactions [87]-[89]. For example, the addition of Al_2O_3 supported Cu-Ni enhances the catalytic activity for carbon dioxide hydrogenation [87]. In steam reforming of methane, the interaction between Cu-Ni enhances water gas shift reaction and resulting in enhancement of overall reaction [88]. It was also reported that SiO₂ supported bimetallic Cu-Ni enhances the rate of hydrogen production up to 80% compared to that obtained from Ni supported on SiO₂ in methane decomposition [89]. However, study on bimetallic Cu-Ni catalyst for photocatalytic reaction was limited.

Study on bimetallic photocatalyst for reduction of nitrate was reported by Gao and co-workers [90]. Various metals, Pt, Pd, Cu, and Ni, were incorporated on the surface of TiO₂ in forms of monometallics Pt/TiO₂, Pd/TiO₂, Cu/TiO₂, Ni/TiO₂, and bimetallics Pt-Cu/TiO₂, Pd-Cu/TiO₂, and Cu-Ni/TiO₂. Among these photocatalysts, Cu-Ni/TiO₂ displayed the best photocatalytic activity as it has the highest yield of nitrite and ammonia. In addition, the Cu-Ni/TiO₂ bimetallic photocatalyst was studied with different metal loading and various Cu:Ni mass ratio and the highest activity was achieved for 4wt% Cu-Ni/TiO₂ photocatalyst with 3:1 Cu:Ni mass ratio. Better photocatalytic activity was found as the result of effective separation of photogenerated electrons-holes. The presence of two different metals displays synergetic effect by trapping both holes and electrons thus preventing their recombination. The well dispersed metal dopants on the surface of TiO₂ also gave the beneficial effect in improving the photocatalytic activity of bimetallic Cu-Ni/TiO₂.

2.5 Sacrificial Agent

Adding sacrificial agent into water for photocatalytic hydrogen production has been reported as an effective method to prevent the recombination of photogenerated electrons-holes. In this system, the photogenerated holes react irreversibly with the sacrificial agent (electron donor or hole scavenger) thus suppressing the photogenerated electrons-holes recombination.

In order to gain an effective irreversible reaction of photogenerated holes with sacrificial agent, the sacrificial agent must be easily oxidized. For this reason, organic compound is generally used as sacrificial agent. Formic acid, acetic acid, methanol, 2-propanol, formaldehyde, sucrose, and glycerol have been reported as effective sacrificial agent for photocatalytic hydrogen production [91]-[96]. Zielinska *et al.* [91] investigated the use of different sacrificial agent, namely formic acid, acetic acid, methanol, 2-propanol, and formaldehyde for photocatalytic hydrogen production. Among these organic compounds, formic acid was found to be the most effective sacrificial agent. In the presence of methanol and propanol, photocatalytic hydrogen production involves stepwise reaction with various intermediate products. The presence of intermediate products further caused the competition between those products with photogenerated holes thus decreasing the hydrogen production rate.

Instead of using expensive sacrificial agents, researchers have attempted to develop a new system of simultaneous photocatalytic hydrogen production with photocatalytic degradation of organic wastes and pollutants. Patsoura *et al.* [97] proved that the addition of azo dye as electron donor enhanced hydrogen production rate. The decomposition of electron donor occurred simultaneously with hydrogen production and its rate was proportional to hydrogen production. Another work by Patsoura *et al.* [98] reported on the photocatalytic hydrogen production with simultaneous pollutant degradation. The reaction was conducted using Pt/TiO_2 in the presence of methanol, ethanol, propanol, butanol, formic acid, and acetaldehyde. It was found that the highest amount of hydrogen evolved was obtained with the addition of ethanol. The photocatalytic reaction in the presence of sacrificial agent led to formation of intermediate products from the degradation process.

Once the degradation process has completed, the amount of hydrogen evolved was found to decrease, comparable to that obtained when pure water was used. The amount of hydrogen evolved and carbon dioxide produced are in good agreement with the initial concentration of the organic pollutant added to the solution. It was also found that in the photocatalytic hydrogen production in the presence of organic compound (sacrificial agent) the overall photocatalytic hydrogen production might be similar to the photoinduced reforming of organic compound at room temperature and atmospheric pressure.

The addition of alcohol as sacrificial agent for photocatalytic hydrogen production has been extensively studied and reported in many papers [99]-[101]. Strataki *et al.* [102] observed the photocatalytic hydrogen production from water-ethanol solution. Herein, a thin film of Pt/TiO_2 was used as photocatalyst. It was proved that the presence of ethanol as electron donor and hole scavenger could enhance the amount of hydrogen evolved with 32% overall efficiency. On the photocatalytic hydrogen production in the presence of glycerol [100], [101], it was found that glycerol not only improved the photocatalytic hydrogen generation but also degraded into useful products. Some intermediate products, namely glyceraldehyde, and glycolic acid were formed. The formation of these products provided added economical value from photocatalytic hydrogen production.

2.6 Glycerol Oxidation

Glycerol is an organic compound which is commonly used in pharmaceutical, food, tobacco, paint, pulp and paper, leather, and textile industries [103]. It is colourless, odourless and viscous. It is widely synthesized by microbial fermentation or chemical synthesis from petrochemical feedstock. However, glycerol may also be formed as a byproduct from saponification in soap making and transesterification of biodiesel production [104].

The significant growth in biodiesel production led to excess of glycerol production as reported by most of European countries [103]. Therefore, development of technology to form value-added products from glycerol is crucial.

The conversion of glycerol into simpler carbonyl compounds has attracted much attention from researchers [105]-[112]. A range of possible products may be formed from glycerol oxidation depending on its selectivity as displayed in Figure 2.4. Two general paths are proposed with mesooxalic acid or oxalic acid as the final products. The first path is through the formation of dihydroxyacetone followed by the formation of hydroxypiruvic acid, glycolic acid, and then finally oxalic acid. The second path is through glyceraldehyde formation followed by glyceric acid formation. However, glyceric acid might form either hydroxypiruvic acid or tartronic acid. Tartronic acid can further oxidized to form mesooxalic acid and oxalic acid. These oxidized products are used in numerous industrial applications. Dihydroxyacetone, generally known as DHA is used in pharmaceutical manufacturing as an ingredient in sunless tanning product and as a synthon in organic synthesis. Glycolic acid is also used in pharmaceutical industry to promote skin repair and anti-aging agent. Glyceric acid is used for synthesis of optical isomers from amino acids such as L-serine, dihydroxyacetone is used as a synthon in the cosmetics industry; and hydroxypyruvic acid is a flavor component in cheese [113].

Glycerol oxidation over metal-supported catalyst has been widely investigated by researchers and it has been shown that selectivity of the desired products was mainly affected by the reaction conditions (pH and temperature), morphology, and particle size of catalyst.

Bianchi *et al.* [106] reported the oxidation of glycerol over monometallic and bimetallic Au, Pt, and Pd based catalysts prepared by applying different techniques of sol-gel method. It was found that bimetallic catalyst showed better performance compared to that of monometallic.

Bimetallic Au-Pd/C showed better selectivity to glyceric acid, more than 90%, with Pd promoting further oxidation to form tartronic acid. On the other hand, bimetallic Au-Pt/C showed lower selectivity to glyceric acid compared to that from Au-Pd/C. The presence of a second metal (Pt) promotes further oxidation to glycolic acid. It was also found that different catalyst preparation method did not significantly affect selectivity to glyceric acid as it was proved by similar catalytic results.



Figure 2.5 Reaction network of glycerol oxidation [106]

Claus research group [110], [111], [114] investigated glycerol oxidation over monometallic and bimetallic Au based catalyst prepared with different techniques, gold-sol and deposition precipitation. Different reaction conditions such as temperature, pressure, stirring speed, and base concentration were also studied. It was found that different catalyst preparation techniques greatly affect the activity of catalyst. The catalyst prepared with gold-sol technique with THPC (tetrakishydroxymethyl-phosphonium chloride) as reducing agent displayed the best catalyst activity among the others (precipitation method and gold-sol method with NaBH₄ as reducing agent). THPC stabilized the colloid of gold solution which leads to the formation of smaller particle size thus leads to more effective glycerol oxidation. The smaller particle size formed led to selectivity to glyceric acid up to 75%. The presence of second metal was also affected glycerol oxidation. In the presence of Pt as second metal it was found that glycerol conversion increased to almost 100% with selectivity to glyceric acid increased from 26% to 36%. The formation of alloy Au-Pt is believed to give the beneficial effect on enhancement of glycerol oxidation. In term of reaction conditions, it was found that higher temperature enhanced catalytic activity of glycerol oxidation while the pressure did not affect it.

Recent study on glycerol oxidation has reported that glycerol oxidation might be performed in photocatalytic reaction as investigated by Augugliaro *et al.* [115].

In this study, they used synthesized and commercial TiO_2 for photocatalytic glycerol oxidation under UV-light irradiation (125 W Hg pressure lamp). The photocatalytic oxidation was performed in two different reactor, annular and cylindrical photoreactor. Prior to photocatalytic reaction, oxygen gas was bubbled into the reactor until thermodynamically equilibrated. It was reported that cylindrical photoreactor displayed better performance compared to that of annular photoreactor, the global selectivity to glyceraldehyde, formic acid, dihydroxyacetone and CO₂ had an average value of 35 mol% with respect to the converted glycerol. While for cylindrical photoreactor, the global selectivity had an average value of 45 mol% with respect to the reacted glycerol. It was also found that Degussa P 25 TiO₂ was the most active photocatalyst for this reaction.

2.7 Bandgap Energy Determination

Bandgap energy is an important property for photocatalyst relating its ability to absorb photon. The absorption spectra of photocatalyst is commonly characterized by UV-Vis spectroscopy. A UV-Vis spectrophotometer is also equipped with an integrating sphere to measure the reflectance of the photocatalyst. Further, the reflectance spectra was used to determine its bandgap energy by applying Kubelka-Munk theory. The theory proposed the behaviour of light traveling inside the light scattering specimen [116]. It allows calculation of reflectance from a layer that both scatters and absorbs light. To apply this model, a sample must be sufficiently thick to make sure that all the incident light is absorbed or scattered before reaching the back surface. 1-3 mm thickness is generally sufficient to meet this condition [117]. The model is shown as follow:

$$F(R_{\infty}) = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} = \frac{K}{S}$$
(2.2)

where,

K is the absorption coefficient,

S is the scattering coefficient and

 R_{∞} is the reflectance of the sample at the infinite thickness.

Bandgap energy of photocatalyst is determined from extrapolation of Tauc's Plot, a plot of $(F(R).h\nu)^{1/2}$ as the function of photon energy (h ν) [118]. Based on Planck-Einstein equation, photon energy derived using the following formula:

$$E = \frac{hc}{\lambda}$$
(2.3)

where,

h is Planck's constant = $4.13566733 \times 10^{-15} \text{ eV}.\text{s}$

c is the speed of light = $2.99792458 \times 10^8 \text{ ms}^{-2}$

 λ is wavelength

CHAPTER 3 METHODOLOGY

In this study, monometallic (Cu/TiO₂, Ni/TiO₂) and bimetallic photocatalysts (Cu-Ni/TiO₂) were prepared by precipitation method using sodium hydroxide, NaOH (Merck, 95%) as the precipitating agent. TiO₂ Degussa P25 was used as support while copper(II) nitrate trihydrate, Cu(NO₃)₂.3H₂O (Acros, >98%), and nickel(II) nitrate hexahydrate, Ni(NO₃)₂.6H₂O (Acros, >98%) were used as metal precursors. Glycerol (systerm, 95%) was used in photocatalyst preparation and also as sacrificial agent in reaction study. The reaction studies were conducted in two different media: distilled water (H₂O) and a mixture of distilled water and glycerol (H₂O+gly).

3.1 Photocatalyst Preparation and Pretreatment

A series of photocatalysts were prepared via precipitation method with the following research parameters: calcination temperature, calcination duration, Cu:Ni mass composition, and total metal loading, as shown in Figure 3.1.

Appropriate amount of Cu(NO₃)₂.3H₂O and Ni(NO₃)₂.6H₂O were weighed and dissolved in 200 mL distilled water. Glycerol was added to this solution and continuously stirred using a magnetic stirrer. The amount of glycerol was fixed at 2:1 mol ratio of glycerol:total metal. Then TiO₂ support was added into the solution under vigorous stirring. After 1 h of stirring, the suspension was precipitated with 0.25 M NaOH until pH=12 and the mixture was aged for 24 h. After that, the mixture was filtered and dried overnight at 75 °C.

Prior to calcination, thermal gravimetric analysis (TGA) of the photocatalysts were carried out using Perkin Elmer (Pyris 1 TGA) instrument in order to estimate appropriate calcination temperature.



Figure 3.1 Design of experiment

Denotation for the photocatalyst: awt%_xCuyNi_T_R, where "a" represents total metal loading on the photocatalysts in wt% while "x" and "y" represent the mass composition of copper and nickel, respectively, where x+y=10. "T" indicates calcination temperature in °C while "R" indicates duration of calcination in hour. For example, the bimetallic 10wt%_5Cu5Ni_180_0.5 represents 10wt% total metal loading, with 5:5 Cu:Ni mass composition, calcined at 180°C for 0.5 h. As for the monometallics, 10wt%_10Cu_200_1 represents 10wt% Cu metal loading, calcined at 200 °C for 1 h. The schematic diagram for photocatalysts preparation is presented in Figure 3.2.



Figure 3.2 Schematic diagram for photocatalyst preparation

3.1.1 Effect of Calcination Temperature and Duration

Study on the effect of calcination temperature and duration was conducted using a photocatalyst with 10wt% total metal loading and Cu:Ni mass composition of 5: 5.

Based on the thermograms obtained from TGA of the raw photocatalysts, calcination was conducted at 180, 200, and 250 °C for 0.5 h, 1 h and 2 h.

The photocatalyst that displayed the best performance for hydrogen production from water (Section 3.2) in terms of calcination temperature and duration was selected for the next study in Section 3.1.2.

3.1.2 Effect of Cu:Ni Mass Composition

Photocatalysts with 10wt% total metal loading were prepared with different Cu:Ni mass composition, 9:1; 7:3; 5:5; 3:7; and 1:9. As for comparison, monometallics 10wt% Cu/TiO₂ and 10wt% Ni/TiO₂ were also prepared. The amount of chemicals required in preparing the photocatalysts with desired Cu:Ni mass composition were presented in Table 3.1. Example of calculation for the amount of chemical used is given in Appendix A.

Chemicals	Cu:Ni Mass Composition						
	10:0	9:1	7:3	5:5	3:7	1:9	0:10
Mass of Cu(NO ₃) ₂ ·3H ₂ O ₁ (g)	3.802	3.422	2.661	1.901	1.141	0.380	0
Mass of Ni(NO ₃) ₂ ·6H ₂ O, (g)	0	0.495	1.486	2.476	3.467	4.458	4.953
Mass of TiO ₂ , (g)	9.000	9.000	9.000	9.000	9.000	9.000	9.000
Total Volume of glycerol, (mL)	3.8	2.3	2.4	2.4	2.4	2.5	4.8
Total Volume of distilled water, (mL)	200.0	200.0	200.0	200.0	200.0	200.0	200.0
Total Volume of NaOH 0.25M, (mL)	140.0	140.0	140.0	140.0	140.0	140.0	140.0

Table 3.1 Summary of the amount of chemicals required to prepare 10g, 10wt% photocatalyst with different Cu:Ni mass composition

Based on the results from Section 3.1.1, the best pretreatment conditions for calcination was 200 °C for 1 h. Therefore, all the photocatalysts were calcined at 200 °C for 1 h.

The photocatalyst that produced the highest amount of hydrogen gas during reaction in different Cu:Ni composition (Section 3.1.2) was selected for further studies on the effect of total metal loading (Section 3.1.3).

3.1.3 Effect of Total Metal Loading

Based on the results from Section 3.1.2, the best Cu:Ni composition was 9:1. In order to study the effect of total metal loading on the photocatalytic performance, photocatalysts with Cu:Ni mass composition of 9:1 were prepared with different metal loading (5, 10, and 15wt%). All the photocatalysts were calcined at 200 °C for 1 h. Preliminary results for H₂ production indicated that 10wt% total metal loading produced photocatalyst with the best performance. Therefore, for comparison, photocatalysts with 9wt% and 11wt% metal loadings were also prepared. The amount of chemicals required in preparing the photocatalysts with the desired metal loading are presented in Table 3.2.

Table 3.2 Summary of the amount of chemicals required to prepare 10g photocatalyst of 9:1 Cu:Ni mass composition with different metal loading

Chemicals	Metal Loading, wt%				
	5	9	10	11	15
Mass of Cu(NO ₃) ₂ ·3H ₂ O, (g)	1.711	3.080	3.422	3.764	5.133
Mass of Ni(NO ₃) ₂ ·6H ₂ O, (g)	0.248	0.446	0.495	0.545	0.743
Mass of TiO_2 , (g)	9.500	9.100	9.000	8.900	8.500
Total Volume of glycerol, (mL)	1.3	2.1	2.3	2.5	3.5
Total Volume of distilled water, (mL)	200.0	200.0	200.0	200.0	200.0
Total Volume of NaOH 0.25M, (mL)	140.0	140.0	140.0	140.0	140.0

3.2 Photocatalytic Activity Study

The set up for photocatalytic studies consists of a light source, a multiport reactor and water displacement unit. A 500 W halogen lamp was used as the visible light source which was positioned at a distance of 15 cm on top of the multiport reactor. The intensity of the radiation was 413 Wm⁻². In order to keep the constant temperature at room temperature (30 °C), a fan was used as cooling system to hinder the effect of heat generated from the light source (500 W halogen lamp). The multiport has four ports (40 mL each) and each port is connected to a water displacement unit for measuring gas volume. Figure 3.3 shows the set up for the photocatalytic reaction.



Figure 3.3 Photocatalytic Reaction Setup

3.2.1 Distilled Water as Reaction Medium (H₂O)

The photocatalytic reaction was conducted at room temperature and atmospheric pressure. A known amount of photocatalyst (0.1g) in powder form was suspended in distilled water (8.0 mL) and placed in the multiport reactor. The amount of gas evolved was collected and monitored for 2 hours. For identification, the gaseous product was collected in a gas sampling bag and analysed using a Gas Chromatograph (Agilent 6890 series GC system) with 5A molecular sieve column (capillary 45.0m x 530 μ m x 25 μ m) and equipped with a thermal conductivity detector. Helium gas was used as the mobile phase with spilt ratio of 10:1, pressure of 0.619 bar, 6.0 mL min⁻¹ flowrate, and 46 cm s⁻¹ average velocity. The oven temperature was set at 60 °C and 11 min runtime. The GC was calibrated using a standard gas (H₂ and O₂). The standard gas was injected into the GC to determine the retention time and peak area corresponding to its amount.

3.2.2 Mixture of Distilled Water and Glycerol as Reaction Medium (H₂O+gly)

The effect of glycerol as sacrificial agent on photocatalytic hydrogen production as well as for the production of oxidized products were studied. These oxidized products remained in the aqueous solution. The photocatalytic studies were conducted using similar experimental setup as in Figure 3.3 with slight modification. Prior to the connection to the water displacement unit, the gas evolved was passed through some calcium hydroxide Ca(OH)₂ solution to trace the presence of carbon dioxide gas (CO₂) that might be released. Positive indication of the presence of CO₂ is by the formation of insoluble calcium carbonate (CaCO₃).

The reaction was conducted by adding 95% glycerol to 8.0 mL of distilled water followed by 0.1g of photocatalyst into the mixture. The volume of glycerol added was varied from 2.0, 4.0, 6.0, and 8.0 mL. The best composition of glycerol and water $(H_2O + gly)$ was selected for Sections 3.2.3 and 3.2.4.

The reaction was conducted at room temperature and atmospheric pressure. The gaseous product was analysed by using Gas Chromatograph (Agilent 6890 series GC system, He gas) with similar conditions as in Section 3.2.1. The oxidized products from glycerol were analyzed using high-performance liquid chromatograph analysis (HPLC Agilent 1100 series) equipped with auto sampler. The analysis was carried out using a ICE-ORH-801 column (Transgenomic) with 0.01 N H₂SO₄ as eluent. The flowrate of eluent was set at 0.8 mL.min⁻¹. The standard solution was prepared in the eluent with different concentrations. The injection volume was 20 μ L and the column temperature was set at 40 °C [114]. Some intermediate products of glycerol oxidation i.e. glycolic acid, formic acid, oxalic acid, mesooxalic acid and glyceraldehyde were used as standards for analysis and the corresponding results were used for qualitative and quantitative sample analysis.

3.2.3 Kinetic Study

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The kinetic study was conducted to determine the value of the apparent rate constant (k) and the order of reaction (n).

The kinetics rate was modeled as the function of photocatalyst loading as described below:

$$r_o = \frac{d \left[H_2\right]_o}{dt_o} = k \left[photocatal \, yst\right]^n \tag{3.1}$$

By linearizing equation 3.1,

$$\ln r_o = n \ln [photocatalyst] + \ln k$$
(3.2)

Plotting $\ln r_0$ against $\ln [$ photocatalyst], the value of k and n can be estimated from the intercept and the slope, respectively.

The amount of H₂ produced from 8.0 mL of H₂O was investigated by varying the amount of photocatalyst added into the system (0.025, 0.050, 0.100, 0.200, 0.400, 0.600, 0.800, and 1.000 g). The photocatalyst used for this study was $10wt\%_9Cu1Ni_200_1$. Similar procedure was employed for the (H₂O+gly) system where 2.0 mL of glycerol was added to 8.0 mL of H₂O.

Table 3.3	Reaction	conditions	for	kinetic	study
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Condition	H ₂ O	$H_2O + gly$	
Concentration of photocatalyst, (g/L)	3.1; 6.3; 12.5; 25.0; 50.0; 75.0; 100.0; 125.0	3.1; 6.3; 12.5; 25.0; 50.0; 75.0; 100.0; 125.0	
Water volume, (mL)	8.0	8.0	
Glycerol volume, (mL)	0	2.0	

3.2.4 Prolonged Illumination

In order to investigate the activity of the photocatalyst for prolong illumination, photocatalytic reaction was investigated using 0.1 g 10wt%_9Cu1Ni_200_1 for 50 h reaction.

The reaction was conducted in 8 mL distilled water (H_2O) and also a mixture of distilled water and glycerol (H_2O+gly), similar to the procedure in Section 3.2.3.

3.3 Photocatalyst Characterization

Photocatalyst characterization was carried out in order to determine the bulk and surface properties of the photocatalysts using Thermogravimetric Analysis (TGA), Powder X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Field-emission Scanning Electron microscopy – Energy Dispersive X-ray (FESEM-EDX), Diffuse Reflectance UV – visible spectroscopy (DR-UV-Vis), Brunauer-Emmet-Teller (BET), and Temperature Programmed Reduction (TPR).

3.3.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were carried out to determine the thermal stability of photocatalysts. The thermograms obtained were further used to determine the thermal decomposition of compounds present in the photocatalysts in order to estimate the appropriate calcination temperature and duration. The analyses were conducted using Perkin Elmer TG (Pyris 1) system under the 20mL.min⁻¹ air flow, from 30 °C -800 °C at ramp rate 10 °Cmin⁻¹.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy was carried out to identify species (functional group) present in the photocatalysts before and after calcination. The analyses were conducted using Shimadzu 8400S Spectrophotometer.

A small amount of photocatalyst was grained together with 200 mg of IR-grade KBr and pressed into pellet using a hydraulic hand press. Later the pellet was placed in the sample holder and scanned from 4000 cm⁻¹ to 400 cm⁻¹ with 1.2 cm⁻¹ resolution.

3.3.3 Field Emission Scanning Electron Microscopy – Energy Dispersive X-ray (FESEM-EDX)

Field-emission Scanning Electron microscopy is one of the analysis method used to determine the surface properties of the photocatalyst such as crystallite shape, size, and metal dispersion. When coupled with EDX, it also provides qualitative elemental analysis and element localization on samples can be analyzed.

The FESEM-EDX analyses were conducted using Zeiss Supra 35VP. First, the photocatalyst was coated with platinum. Further, the coated photocatalyst was placed into the instrument for scanning. The analyses were performed under the following conditions:

EHT = 15 kV Working distance = 2-4 mm Magnification = 80 KX

3.3.4 Diffuse Reflectance UV-Visible Spectroscopy (DR-UV-Vis)

The reflectance spectra of the photocatalysts were recorded using Shimadzu Lambda 900 spectrophotometer, equipped with integrating sphere. A few grams of photocatalysts were pressed and placed in a disc (3mm thick). Later, the photocatalysts were placed in the sample holder and the spectra were recorded at 190 - 800 nm. Ba₂SO₄ powder was used as an internal reference. Reflectances spectra were collected as Rsample/Rreference and then plotted applying Kubelka-Munk Theory in order to determine bandgap energy as mentioned in Section 2.6.

3.3.5 Surface Area and Porosity Analysis

Surface area and porosity are important properties of the photocatalyst that could be related to the activity and stability of the photocatalysts. In this study, isotherm adsorption of N_2 onto the photocatalyst employing Brunauer-Emmet-Teller method was used to calculate the specific surface area of the photocatalysts. This method is based on multipoint nitrogen adsorption-desorption principle.

The nitrogen adsorption isotherm is determined by cooling the sample to the boiling point of liquid nitrogen (-77.3 K). The known amount of nitrogen subsequently adding stepwise until the saturation pressure of nitrogen is reached. The number of gas molecules adsorbed on the surface increases with each incremental pressure. The pressure at which adsorption equilibrium occurs is measured and the universal gas law is applied to determine the quantity of gas adsorbed. The desorption isotherm is determined by desorbing nitrogen from the saturated sample in a stepwise mode with the same precaution taken to ensure desorption equilibration as applied under adsorption condition. The BET surface area of the photocatalysts was determined using a surface analyzer (Micrometrics ASAP 2000). For each analysis approximately of 0.2-0.3 g of sample was weighed into a sample tube with filler rod inside. Prior to the analysis, each photocatalyst sample was degassed at 120 °C overnight to remove impurities and moisture. The dewar flask cold trap was filled with liquid nitrogen to trap impurities in the manifold. After degassing, the sample was left to cool to ambient temperature and the tube was removed from the degassing port. Since the sample is under vacuum, the tube is backfilled with nitrogen gas before it can be removed safely.

The sample tube was reweighed to determine the actual sample mass for the analysis. Subsequently, it was connected to the analysis port and secured by a connector nut, ferrule and o-ring. The isothermal jacket was placed around the sample tube to maintain liquid nitrogen level on both the sample tube and the pressure measurement tube. The sample cell was immersed in liquid nitrogen in a dewar flask on an elevator. The sample information was further fed into the software prior to the analysis.

The surface area and pore volume were calculated using the Brunauer-Emmett-Teller (BET) method, while the pore size distribution was determined from the desorption branch of the desorption isotherm by the Barrett-Joyner-Halenda (BJH) method.

3.3.6 Temperature Programmed Reduction (TPR)

The temperature programmed reduction studies were conducted in order to determine the reducibility of the photocatalysts and metal dispersion in photocatalysts. In addition, the supported precursor phases and their interactions with the support can be identified. The TPR measurements were carried out using Thermo Finnigan TPDRO 1100 equipment. Samples were loaded in a quartz U-tube reactor and placed between two layers of quartz wool. Then, the sample was placed in a holder surrounded by an electric furnace. Approximately of 0.1-0.2 g of sample was used for each measurement. Prior to analysis, the sample was pretreated under nitrogen with a flow rate of 20 mL min⁻¹ by heating from room temperature to 110 °C with a ramp rate of 10 °C min⁻¹. Finally the sample was held at 110 °C for 10 minutes to eliminate moisture and impurities before cooling to room temperature. After pretreatment, TPR analysis was carried out in 5% H₂ in N₂ with a flow rate of 20 mL min⁻¹. Sample was heated from 40 °C-800 °C with a ramp rate of 10 °C min⁻¹ and holding at 800 °C for 30 minutes. The reduction profile was displayed as a plot of hydrogen consumption versus temperature.

3.3.7 Powder X-ray Diffraction (XRD)

X-Ray Diffraction Analysis (XRD) is the primary tool for investigating the structure of crystalline materials, from atomic arrangement to crystallite size and imperfections. The phases present in the photocatalysts and degree of crystallinity were investigated using XRD.

All prepared photocatalysts powder were subjected to XRD (Bruker D8 Advance) with Cu K_{α} radiation (40 kV, 40 mA) at 20 angles from 10° to 80°, with a

scan speed of 4° min⁻¹. The unknown component can be identified by using the standard diffraction data.

Particle sizes (D) of photocatalyst was estimated using the Scherrer formula [119]:

$$D = \frac{K\lambda}{FWHM\cos\theta}$$
(3.3)

where,

K = Scherrer constant

FWHM = full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern

 λ = wavelength of rays

 θ = diffraction angle of rays

The Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9 [120].

The composition of anatase and rutile phase present in photocatalysts was calculated using the following formula [121]:

$$\omega_A = \frac{I_A}{I_A + 1.265 I_R} \times 100\%$$
 3.4

 $\omega_R = 1 - \omega_A \tag{3.5}$

where,

 $\omega_A = \text{the composition of anatase phase, }\%$ $\omega_R = \text{the composition of rutile phase, }\%$ $I_A = \text{maximum intensity of anatase phase, Cps}$

 I_R = maximum intensity of rutile phase, Cps

CHAPTER 4

RESULTS AND DISCUSSIONS

A number of photocatalysts have been prepared and tested for photocatalytic hydrogen production from water as well as from water in the presence of glycerol as sacrificial agent. Their physical and chemical properties were determined using various instruments as described in Section 3.3.

4.1 Pretreatment of Photocatalyst

A typical thermogram representating the bimetallic 10wt%_5Cu5Ni raw photocatalysts is presented in Figure 4.1. The TG curve showed two decomposition steps, 30 °C to 180 °C and 180 °C to 400 °C. The total weight loss is about 2.4% at the first decomposition step that indicates the dehydration of the precursors and evaporation of physically absorbed substances [122].



Figure 4.1 Thermal decomposition of 10wt%_5Cu5Ni raw photocatalyst

The second decomposition step at 180 °C to 400 °C showed about 11.5% total weight loss attributed to the decomposition of metal hydroxide, Ni(OH)₂ and Cu(OH)₂, to metal oxide, NiO and CuO, respectively [92], [123], [124]. Thus, proposed decomposition steps for the fresh photocatalyst are as follow:

The straight horizontal line at 400 °C indicates that no further decomposition occurs and thermal stability has been reached. Based on the TGA results, three calcination temperatures were selected, 180 °C, 200 °C, and 250 °C, for different duration: 0.5 h, 1 h and 2 h. This condition was selected based on assumption that thermal stability of photocatalyst might be achieved for longer calcination duration at lower temperature (< 400 °C) as later proved by FTIR (Section 4.3.1) and TPR analyses (Section 4.3.5).

4.2 Photocatalytic Activity of Cu/TiO₂, Cu-Ni/TiO₂, and Ni/TiO₂ Photocatalysts

The photocatalytic reactions were conducted in two different media, distilled water (H₂O) and mixture of distilled water and glycerol (H₂O + gly). Herein, glycerol was studied in terms of its function as a sacrificial agent as well as for the production of value-added derivatives from glycerol.

4.2.1 Distilled Water as Reaction Medium (H₂O)

The amount of hydrogen evolved during photocatalysis in water is strongly affected by physical and chemical properties of the photocatalysts. Surface area, calcination temperature and condition, metal dispersion as well as bandgap energy have been widely studied as the main factors that strongly affect the activity of photocatalyst [124]-[126]. In this study, a series of monometallic Cu/TiO₂, Ni/TiO₂, and bimetallic Cu-Ni/TiO₂ photocatalysts were prepared to study the effects of calcination temperature and duration, copper to nickel mass composition, and total metal loading on their photocatalytic activities (Sections 3.1.1, 3.1.2, and 3.1.3). The amount of hydrogen evolved for each photocatalyst is displayed in Appendix B.

The photocatalytic reaction was monitored for 2 h and the amount of hydrogen evolved was measured every 10 minutes. Figure 4.2 shows the volume of hydrogen evolved as a function of time for $10wt\%_9Cu1Ni_200_1$. It is clearly seen that the amount of hydrogen evolved started to reach steady state at t = 80 to t = 120 minutes. All the other photocatalysts displayed similar hydrogen evolution pattern as $10wt\%_9Cu1Ni_200_1$. Therefore, for further studies, the amount of hydrogen evolved from photocatalytic reaction was monitored for 2 h.



Figure 4.2 The amount of hydrogen evolved from 10wt%_9Cu1Ni_200_1 for 2 h reaction.

4.2.1.1 Effect of Calcination Temperature and Duration

Calcination temperature and duration are important factors that affect photocatalytic activity. The calcination temperatures were estimated based on the resulting thermogram in Figure 4.1. 10wt% photocatalysts with 5:5 Cu to Ni mass composition was calcined at 180 °C, 200 °C, and 250 °C for 0.5, 1, and 2 h. Their photocatalytic activities were monitored for 2h and their corresponding results are presented in Figure 4.3.

The activity of bare TiO_2 was also assessed. It is obvious that in comparison with the modified photocatalyst, pure TiO_2 produced the lowest amount of hydrogen, 2.0 mL after 2 h reaction.



Figure 4.3 The average amount of hydrogen evolved from 0.1 g photocatalysts having Cu:Ni mass composition of 5:5 with 10wt% metal loading and calcined at different temperature and duration

Photocatalysts calcined at 200 °C produced the highest amount of hydrogen (5.0 mL) compared to those calcined at 180 °C (4.8 mL) and 250 °C (4.4 mL). Meanwhile, in terms of calcination duration, no clear trend was found.

For photocatalysts calcined at 180°C, the amount of hydrogen evolved increased as the calcination duration increased. The highest amount of hydrogen evolved was obtained with photocatalyst calcined for 2 h (4.8 mL), followed by 1 h (4.4 mL) and 0.5 h (3.3 mL). However, photocatalysts calcined at 200 °C, displayed a different trend. Better performance was observed after 1 h calcination with 5.0 mL of hydrogen evolved. Photocatalysts with shorter calcination duration (0.5 h) resulted in only 3.3 mL hydrogen, similar to that obtained from photocatalyst calcined at 180 °C for 0.5 h. However, no improvement in the performance was observed for longer calcination time (2 h). A different trend was displayed by photocatalysts calcined at 250 °C. As the calcination duration increased from 0.5 h to 1 h, hydrogen evolved increased abruptly from 2.4 mL to 4.4 mL. However, longer calcination duration (2 h) resulted in decreased hydrogen production (3.4 mL).

The decreased in amount of hydrogen evolved as the calcination temperature increased might be due to the growth and agglomeration of particles promoting bigger particle size as proposed by Singto *et al.* [127]. As a result, the surface area of photocatalyst decreased and subsequently the activity of the photocatalyst decreased [125]. Based on the amount of H_2 produced, calcination at 200 °C for 1 h, are conditions selected for further studies on other experimental parameters.

4.2.1.2 Effect of Cu:Ni Mass Composition

The mass composition of metals in a bimetallic catalyst plays significant role in catalytic activity [127]. In this study, a total metal content of 10wt% was fixed, and the photocatalysts had undergone calcination at 200 °C for 1 h. The only variable was mass composition of Cu:Ni (9:1, 7:3, 5:5, 3:7, 7:3, and 1:9). For comparison, 10wt% monometallic 10wt% Cu/TiO₂ and 10wt% Ni/TiO₂ were also studied. The corresponding results were presented in Figure 4.4.

It is clearly seen that the maximum hydrogen production was obtained from 10wt%_9Cu1Ni_200_1, with 6.1 mL H₂. For the bimetallic photocatalysts, a decrease in Cu content led to lower hydrogen evolution. Meanwhile, for monometallic 10wt%

Cu/TiO₂ and 10wt% Ni/TiO₂, the activities were found to be lower than those of some bimetallic Cu-Ni/TiO₂ photocatalysts.

On the surface of TiO₂, Cu²⁺ acts as both hole and electron traps due to its energy level which is between the conduction band and the valence band of TiO₂ [16], [66], [72], [73], [129], [130]. On the other hand, due to its energy level being nearer to the valence band of TiO₂, Ni²⁺ acts as hole trap [80], [129], [131]. The electrochemical energy levels of Cu²⁺ and Ni²⁺ with respect to TiO₂ are presented in Figure 4.5.



Figure 4.4 The average amount of hydrogen evolved from 0.1 g photocatalysts having 10wt% metal loading with different Cu:Ni mass composition calcined at 200 °C for 1h



Figure 4.5 Electrochemical energy levels of Cu²⁺ and Ni²⁺ with respect to TiO₂

During irradiation, Cu^{2+} traps hole and forms Cu^{3+} (Equation 4.5). The hole trap then migrate (Equation 4.7) or recombine with the mobile electron from the conduction band of TiO₂ (Equation 4.10 and 4.11). However, since Cu^{2+} also acts as electron trap, the recombination reaction with mobile electron was prevented. As a result, Cu^{2+} further reacts with hole and form Cu^+ (Equation 4.4). The hole embodied in Cu^{3+} has a longer lifetime due to the immobilized electron trap in Cu^+ . On the other hand, electron trapping is not favorable for Ni²⁺. Therefore, after hole trapping (Equation 4.6), Ni²⁺ recombines with the mobile electron thus undergoes recombination reaction (Equation 4.12). These phenomena might explain the inferior performance of monometallic Ni/TiO₂ compared to that of Cu/TiO₂. The processes [19], [20], [26], [80], [129]-[131] are as follow:

- 1. Charge pair generation
- $TiO_2 + h\nu \rightarrow e_{CB}^- + h_{\nu B}^+ \qquad \dots (4.3)$
- 2. Charge trapping
- $Cu^{2+} + e_{CB}^{-} \rightarrow Cu^{+} \qquad \dots (4.4)$
- $Cu^{2+} + h_{\nu B}^{+} \to Cu^{3+}$...(4.5)
- $Ni^{2+} + h_{\nu B}^{+} \rightarrow Ni^{3+} \qquad \dots (4.6)$

3. Charge release and migration

 $Cu^{+} + Ti^{4+} \rightarrow Cu^{2+} + Ti^{3+}$...(4.7)

4. Recombination

$e_{CB}^- + h_{\nu_B}^+ \rightarrow TiO_2$	(4.8)
$Cu^+ + h^+_{\nu B} \to Cu^{2+}$	(4.9)
$Cu^{3+} + e_{CB}^- \rightarrow Cu^{2+}$	(4.10)
$Cu^{3+} + Ti^{3+} \rightarrow Cu^{2+} + Ti^{4+}$	(4.11)
$Ni^{3+} + e_{CB}^- \rightarrow Ni^{2+}$	(4.12)

In bimetallic photocatalysts, the addition of small amount of Ni, enhanced the activity of photocatalyst. 9:1 and 7:3 of Cu:Ni mass composition showed higher activity compared to those of bimetallic photocatalyst with lower Cu content and monometallic photocatalysts. Adding small amount of Ni can enhance the hole traping process thus retarding recombination reaction. However, as the amount of Ni increased, it becomes hole accumulation site. Such hole accumulation further attracted the negatively charged species, either from one embodied in Cu²⁺ (as electron trap) or the mobile electron from the conduction band of TiO₂. Therefore, Ni²⁺ itself becomes the recombination reaction center thus decreasing the activity of photocatalyst.

Since 10wt%_9Cu1Ni_200_1 displayed the best performance, the 9:1 Cu to Ni mass composition was selected for further study.

4.2.1.3 Effect of Total Metal Loading

Photocatalytic hydrogen production was investigated using photocatalysts with Cu:Ni mass composition of 9:1. Total metal loading studied were 5wt%, 10wt%, and 15wt% and the photocatalysts were calcined at 200 °C for 1 h. The corresponding results are displayed in Figure 4.6.



Figure 4.6 The average amount of hydrogen evolved from 0.1 g photocatalysts having Cu:Ni mass composition of 9:1 with different metal loading calcined at 200 °C for 1 h

The results clearly revealed that the hydrogen evolution increased as the metal loading increase from 5wt% (3.0 mL) to 10wt% (6.1 mL). However, as the metal loading further increased to 15wt%, the activity of the photocatalyst decreased. In order to confirm 10wt% metal loading as the optimum value, photocatalysts with 9wt% and 11wt% metal loading were also studied. Both loadings produced lower amount of hydrogen, indicating 10wt% as the optimum metal loading.

There are some possible reasons given for this trend. Incorporation of a metal enhanced the photocatalytic activity by increasing the electrons-holes separation thus inhibiting their recombination reaction [19]. However, as the metal loading increased, the metal becomes the recombination reaction centers as the effect of electrostatic forces from negatively charged metal sites after trapping electrons that attracts the positively charged holes [19], [125]. Blockage of the active sites of TiO₂ may also occur as the effect of excessive coverage which results in limitation of light penetration reaching the surface [19], [50], [51]. Thus the number of photogenerated electrons and holes reduced and subsequently lowered the photocatalytic activity [51]. Furthermore, agglomeration of metal particles as the metal loading increases is believed to decrease the photocatalytic activity of photocatalyst [92].

4.2.2 Mixture of Distilled Water and Glycerol as Reaction Medium (H₂O+gly)

Photocatalytic hydrogen production in the presence of glycerol was conducted using $10wt\%_9Cu1Ni_200_1$ and the corresponding results are presented in Figure 4.7. Glycerol acts as a sacrificial agent and added with different volume (2.0, 4.0, 6.0, and 8.0 mL) into 8.0 mL of H₂O. It is clearly seen that the addition of glycerol greatly enhanced the photocatalytic hydrogen production. The highest amount of hydrogen evolved (9.5 mL) was obtained with the addition of 2.0 mL glycerol, 1.5 times higher compared to that obtained in the absence of glycerol (6.1 mL). However, with further addition of glycerol, the amount of hydrogen evolved slightly decreased.

The higher amount of hydrogen evolved is a result of glycerol acting as the holes scavenger thus the electron – hole recombination reaction diminished, enhancing the photocatalytic hydrogen production [101]. The electrons generated under irradiation collected by the metal present in the photocatalyst thus reduced water to form H_2 . On the other hand, the photogenerated holes further oxidized the glycerol (sacrificial agent) which is more easily oxidized than water.



Figure 4.7 The effect of glycerol addition on photocatalytic hydrogen production using 10wt%_9Cu1Ni_200_1 for 2h reaction

The lower hydrogen amount generated with further increase of glycerol concentration might be caused by the effect of intermediate products formed during the reaction. The existence of intermediates caused the competition of glycerol and the intermediates to react with the photogenerated holes [56]. Increasing initial concentration of glycerol also affected the effectiveness of photons reaching the surface of photocatalyst. Once glycerol is adsorbed on the surface of photocatalyst, its shielding effect might affect the photons absorption to activate the photocatalyst. Consequently, as the concentration of glycerol increased, the photon absorption reduced thus decreasing the photocatalytic reaction [132].

It is obvious that the amount of hydrogen evolved increased as a result from glycerol acting as sacrificial agent and the "additional hydrogen product" from glycerol oxidation. However, the amount of hydrogen evolved decreased on further irradiation until 50 h as displayed in Figure 4.11.

Since glycerol was oxidized by photogenerated holes, the intermediate products from glycerol oxidation were analyzed. The intermediate products such as glyceraldehyde, glycolic acid, and oxalic acid were detected and the amount is presented in Table 4.1. No carbon dioxide gas (CO_2) was detected during photocatalytic reaction as shown by negative indication from calcium hydroxide Ca(OH)₂ solution. It was reported by Daskalaki and Kondarides [134] that complete mineralization of glycerol into carbon dioxide could only occur for prolonged illumination, more than 100 h.

t (h) Glyceraldehy		Glycolic acid	Oxalic acid	
	de	(x 10 ⁻⁴ M)	(x 10 ⁻⁶ M)	
2	1.59	6.79	3.49	
10	6.01	7.07	6.45	
20	7.68	8.72	13.80	
50	13.60	17.4	24.90	

Table 4.1 The amount of intermediate products from glycerol oxidation

It is observed that the amount of intermediate products increased with increasing illumination time. The intermediates reached maximum amount at 50 h reaction with glyceraldehydes and glycolic acid as the main products and small amount of oxalic acid. Trace amounts of other intermediate compounds detected in the liquid phase could not be identified with certainty and therefore were not discussed further. The conversion was about 24.07%. The main intermediate products formed are in agreement with those reported by Li et al. [133] where glyceraldehydes and glycolic acid were the main products from photocatalytic hydrogen production from mixture of water and glycerol.

4.2.3 Kinetic Study

The rate of photocatalytic hydrogen production was studied for distilled water (H_2O) and distilled water in the presence of glycerol (H_2O+gly). The kinetic was investigated as the function of photocatalyst amount as described in Section 3.2.3.

Figure 4.8 showed the initial reaction rate of photocatalytic hydrogen production from (H₂O) with different photocatalyst amount. It is clearly seen that the initial reaction rate increases as the amount of photocatalyst increase until 75 g/L and tends to decrease for further addition of photocatalyst amount. Obviously, there was an optimum value of photocatalyst amount which can give maximum reaction rate. This result was in good agreement with those of various photocatalytic reactions [132], [134]-[139].


Figure 4.8 The effect of photocatalyst concentration on initial reaction rate of photocatalytic hydrogen production from (H₂O)

The maximum value of photocatalyst amount in photocatalytic reaction might be explained as the effect of photocatalyst aggregation and light scattering. Higher amount of photocatalyst provides higher surface area for light absorption which leads to increase reaction rate as it is generally observed for most of photocatalytic reaction [134]. However, at a given intensity of irradiation, the absorption of incident photons is reaching saturated point at a certain amount of photocatalyst. Increasing the dosage of photocatalyst gave a detrimental effect on the reaction as a result of shielding effect and the scattering of incident illumination by the photocatalyst within the reactor [136]. When the photocatalyst dosage exceeds its optimal value, the light penetration to the surface of photocatalyst decreased as the effect of high turbidity, thus reducing the photocatalytic reaction rate [132].

For kinetic calculation, the value of apparent rate constant, k, and order of reaction, n, were determined by plotting ln r_0 and ln [photocatalyst] as displayed in Figure 4.9. k and n values were determined using equation described in Section 3.2.3 and the corresponding results were 0.3195 g^{0.84} L^{0.16} min⁻¹ and 0.160, respectively.



Figure 4.9 Plot of $\ln r_o$ versus $\ln [photocatalyst]$ to determine k and n value for photocatalytic hydrogen production from (H₂O)

The same trend of the effect of photocatalyst concentration on initial reaction rate was also observed for photocatalytic hydrogen production from (H₂O+gly) system where glycerol was added as sacrificial agent. The initial reaction rate tends to increase with addition of photocatalyst until the maximum rate at 75 g/L of photocatalyst as displayed in Figure 4.10.

The values of k and n were determined by applying the same method to determine k and n values for photocatalytic hydrogen production from H₂O as shown in Figure 4.11. The calculated k and n values for photocatalytic reaction in the presence of glycerol were $0.3989 \text{ g}^{0.805} \text{ L}^{0.195} \text{ min}^{-1}$ and 0.195, repectively.



Figure 4.10 The effect of photocatalyst concentration on initial reaction rate of photocatalytic hydrogen production from (H₂O+gly)



Figure 4.11 Plot of ln r_o versus ln [photocatalyst] to determine k and n value for photocatalytic hydrogen production from (H₂O+gly)

Compared to photocatalytic hydrogen production from (H₂O), the values of k and n from (H₂O+gly) system were higher. This phenomenon showed that in the presence of glycerol, the reaction produced more H₂ than that in distilled water.

These results were in a good agreement with the effect of glycerol as sacrificial agent. The presence of glycerol retard the recombination reaction thus increasing the photocatalytic reaction rate.

4.2.4 Prolonged Illumination

Figure 4.12 displayed the activity of $10wt\%_9Cu1Ni_200_1$ for 50 h illumination in (H₂O) and (H₂O+gly) systems. The addition of glycerol showed better performance compared to that of distilled water. The amount of hydrogen evolved kept increasing until 25h (23.2 mL) and 16h (13.2 mL) irradiation for (H₂O+gly) and (H₂O) systems, respectively. However, after those durations, no additional hydrogen evolution was detected. Interestingly, after the light off and on after several hours (at t=15 h for H₂O and t= 23 h for H₂O+gly) sudden increased of hydrogen evolved was detected. This might be caused as the effect of reactant adsorption into the photocatalyst during light off thus increasing the photocatalytic reaction when illumination continued.



Figure 4.12 The total amount of hydrogen evolved for 50 h photocatalytic reaction in (H₂O) and (H₂O+gly) system using 10wt%_9Cu1Ni_200_1

The higher amount of hydrogen evolved from (H_2O+gly) compared to that of (H_2O) system showed that the function of glycerol as sacrificial agent was effective for prolonged illumination.

4.3 Photocatalyst Characterization

4.3.1 Fourier Transform Infrared Spectroscopy (FTIR) Spectra of Photocatalysts

Figure 4.13 exhibits the FTIR spectra of 10wt%_9Cu1Ni_200_1 before and after calcination compared to that of TiO₂. For all the spectra, the broad band around 3400 cm⁻¹ was attributed to O–H stretching, and the peak near 1600 cm⁻¹ to H–O–H bending [140]. These peaks might be due to the physically adsorbed water. The intensity of these peaks (not shown) decreased with the increase in calcination temperature. The intense peak at 1384 cm⁻¹ which referred to nitrate (NO₃) band [140] is observed in raw and calcined photocatalysts.



Figure 4.13 FTIR spectra of a) TiO₂, b) 10wt%_9Cu1Ni_200_1, and c) raw 10wt%_9Cu1Ni

The strong band at 1384 cm⁻¹ is always present indicating that some nitrate anions (NO₃⁻) still remained even after several time washing and calcination at high temperature (723K). Li and Inui [141] also observed the presence of a band at 1384 cm⁻¹ referred to nitrate which is always present when nitrate salts are used as precursors. However, in our study, the present of nitrate anions in photocatalysts did not affect the catalytic activity of the photocatalysts. Another peak around 2400 cm⁻¹ was also found. This peak was attributed to free CO₂ from the atmosphere [140].

4.3.2 Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray (FESEM-EDX) of Photocatalysts

Field Emission Scanning Electron Microscopy (FESEM) is a high-resolution imaging technique used to evaluate the surface morphologies of photocatalyst such as crystallite shape, size, and metal dispersion. Energy Dispersive X-Ray Spectroscopy (EDX) is used to qualitatively and quantitatively analyze the elements present in a selected area of the FESEM image. Analyses were carried out over the photocatalysts: 10wt% 10Cu 200 1, 10wt% 9Cu1Ni 200 1, 10wt% 5Cu5Ni 200 1, and 10wt% 10Ni 200 1 and their FESEM micrographs are displayed in Figures 4.14, 4.15, 4.16 and 4.17, respectively. As it can be seen in all FESEM micrographs, a uniform crystallite shape was obtained for all the photocatalysts. All the photocatalysts tend to have the same morphologies which is spherical with slight agglomeration. The particle size of photocatalyst is about 20-40 nm, in good agreement with the particle size calculated from XRD data using Scherrer equation (Table 4.7, Section 4.3.6).

The agglomeration of photocatalysts might be due to sintering during calcination process. However, from the result depicted in Figures 4.14, 4.15, 4.16, and 4.17 the high metal dispersion is believed to be achieved during photocatalyst preparation. The small clusters of copper and nickel were highly dispersed and incorporated onto TiO_2 surface. The presence of glycerol during precipitation is believed to have contributed to the high metal dispersion.

Glycerol inhibited the aggregation of the metal particle and favors the metal dispersion onto the surface of TiO_2 at the early stage decomposition during calcination [92], [142] as proved by the relatively same particle size of modified and bare TiO_2 (Table 4.7 in Section 4.3.6). Similar morphology with spherical shape and agglomeration of metal particle was also observed by Yoong *et al.* [92] on Cu/TiO₂ photocatalyst. The highly dispersed metal particle on TiO_2 led to better activity thus further enhances the hydrogen production rate [143].

The Energy Dispersive X-Ray Spectroscopy (EDX) analysis permits the identification and dispersion of metal presents in photocatalysts Figures 4.14, 4.15, 4.16, and 4.17 show the elemental mapping of the photocatalysts of 10wt%_10Cu_200_1, 10wt%_9Cu1Ni_200_1, 10wt%_5Cu5Ni_200_1, and 10wt%_10Ni_200_1, respectively. It is obviously seen that the metal are evenly dispersed and shown uniform distribution on photocatalysts. The respective element detected by EDX was shown as the colored spots in the mapping image. The EDX analysis provides proof for the presence of copper and nickel which were not detected by XRD analysis.





Cu mapping

Figure 4.14 FESEM micrograph and EDX elemental mapping of 10wt%_10Cu_200_1





FESEM Micrograph



Ti Ka1



Ti mapping





Cu mapping

Ni mapping









Ni mapping



4.3.3 Diffuse Reflectance UV-Visible Spectroscopy (DR-UV-Vis) of Photocatalysts

DR-Uv-Vis analysis was conducted in order to determine the bandgap energy of the photocatalysts. The DR-UV absorption spectra of bare TiO₂ and photocatalysts with different copper to nickel mass composition is presented in Figure 4.19. The UV-vis spectra of bare TiO₂ showed absorption peaks ranging from 190 nm and 400 nm, similar to that observed by Yoong *et al.* [92] and Anpo *et al.* [144]. The absorption at 323 nm is generally related to the electronic excitation from the valence band O 2p electron to conduction band Ti 3d orbital indicating the Ti is in the form of tetrahedral Ti⁴⁺ species [145]. Comparing to bare TiO₂, the absorption spectra of all photocatalysts showed higher absorption at visible region (400-790 nm.



Figure 4.18 Absorption spectra of photocatalysts with different calcination temperature



Figure 4.19 Absorption spectra of photocatalyst with different Cu:Ni mass composition

According to Escobar *et al.* [146] the broad band appeared in 250-350 nm contributed to the NiO charge transfer band. On the other hand, according to Komova *et al.* [147], a band at 800 nm related to the d-d transition in Cu²⁺ ions in octahedral coordination and a band at 400 nm contributed to the charge transfer Cu-O-Ti. It is clearly seen that $10wt\%_9Cu1Ni_200_1$ showed the highest absorption in the visible region from 390-800 nm, although the absorption at UV region was lower than those of other photocatalysts. The appearance of absorption at visible light range is attributed to the charge transfer transition between the d-electron of the dopant and the conduction band or valence band of TiO₂ [148]. Surface modification of TiO₂ with Cu, Ni, and Cu-Ni, significantly shifted the absorption edge of photocatalyst thus resulted in bandgap energy reduction.



Figure 4.20 Absorption spectra of photocatalyst with different total metal loading

Figure 4.20 represents the absorption spectra of photocatalysts with different total metal loading. Obviously, the absorption spectra at visible region increase as the total metal loading increase. This result was in good agreement with literature. Komova *et al.* [147] observed that the absorption spectra of Cu/TiO₂ photocatalyst shifted to the visible region as the copper content increased. This might be due to the growth of linear size of oxide clusters caused by the copper aggregation. As a result, the axial Cu-O bonds weaken while the in-plane Cu-O bond strengthen and leads to a blue shift d-d transition. It was also reported by Begum *et al.* [149] that increasing the nickel content leads the absorption band to the longer wavelength. However, in the case of calculated bandgap energy, 10wt% photocatalyst showed the lowest bandgap energy, slightly below 15wt% photocatalyst. 5wt% photocatalyst showed the highest absorption in the UV region. However, it showed the lowest performance on photocatalytic hydrogen production as shown in Figure 4.6.

The band gap energies of the photocatalysts were determined from the plot of $(F(R).hv)^{1/2}$ against hv. F(R) is Kubelka-Munk function which derived from reflectance spectra following $F(R) = (1-R)^2/2R$ equation, and hv is the photon energy. The linear extrapolations to calculate bandgap energies are shown in Appendix C. The calculated bandgap energy of photocatalysts with the best fit of Tauc plot extrapolation were presented in Table 4.2. Comparing the bandgap energy with amount of H₂ evolved during reaction, 10wt%_9Cu1Ni_200 1 displayed the results in good agreement. 10wt% 9Cu1Ni 200 1 found to display the lowest bandgap energy (2.78 eV) and produced the highest amount of H₂ (6.1 mL). However, it was found that in this study, low bandgap energy alone did not strongly affect the photocatalytic activity. As can be seen, 10wt% 5Cu5Ni 200 1 with higher bandgap energy (3.05 eV) compared to 10wt% 5Cu5Ni 180 1 (3.04 eV) resulted in higher hydrogen evolution. This phenomenon might be due to the higher surface area of 10wt% 5Cu5Ni 200 1 where the photocatalytic reaction took place. Thus, it can be inferred that a synergetic effect of physical and chemical surface properties of photocatalysts is highly desirable for better photocatalytic hydrogen production.

Photocatalyst	Bandgap energy, eV	H ₂ evolved, mL
Bare TiO ₂	3.16	2.0
10wt%_10Cu_200_1	2.98	5.0
5wt%_9Cu1Ni_200_1	3.15	3.0
10wt%_9Cu1Ni_200_1	2.78	6.1
15wt%_9Cu1Ni_200_1	2.85	4.9
10wt%_7Cu3Ni_200_1	2.98	5.2
10wt%_5Cu5Ni_180_1	3.04	4.4
10wt%_5Cu5Ni_200_1	3.05	5.0
10wt%_5Cu5Ni_250_1	3.14	4.4
10wt%_3Cu7Ni_200_1	3.15	2.4
10wt%_1Cu9Ni_200_1	3.15	2.0
10wt%_10Ni_200_1	2.98	4.3

Table 4.2 Calculated bandgap energy of photocatalysts and pure TiO₂

All the photocatalysts displayed reduction in their bandgap energy which result in better activity compared to that of bare TiO_2 . As described earlier, lower bandgap energy led to higher photocatalytic activity by enhancing the capability of photocatalysts to utilize photon energy from irradiation.

In terms of different calcination temperatures, it was found that the bandgap energy of photocatalysts tend to increase with increasing calcination temperature in agreement with Sakhtivel and co-workers [150] who proposed that the bandgap energy was found to decrease with increasing calcination temperature of the photocatalyst.

4.3.4 Total Surface Area of Photocatalysts

Nitrogen physisorption is a common method used to determine the properties of porous material such as specific surface area, pore volume, average pore diameter, and pore size distribution. The first three parameter were determined by applying BET adsorption theory while the last one; pore size distribution, was determined by applying BJH method.

Modified photocatalysts as well as bare TiO₂ were analyzed as described in section 3.2.8. Isotherm plot of $10wt\%_9Cu1Ni_200_1$ was depicted in Figure 4.21. Isotherm plot shows the amount of N₂ adsorbed by photocatalyst as a function of pressure at set temperature, which was obtained by plotting the volume of N₂ adsorbed (cc/g) against relative pressure (p/p₀). According to IUPAC standard adsorption isotherm, the isotherm plot of $10wt\%_9Cu1Ni_200_1$ shows the Type IV isotherm with H1 hysterisis loop, which indicated capillary condensation in mesoporous adsorbate [151]. For other photocatalysts, the isotherm plots also displayed Type IV with H1 hysterisis loop (Appendix D). Generally, the surface area of modified photocatalysts were higher compared to that of bare TiO₂. This result was in good agreement with some literatures [47], [152]. Colon *et al.* [47] observed the decomposition of nitrate from copper precursor resulted in higher surface area of Cu/TiO₂. Meanwhile, modification of TiO₂ with various transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn) displayed higher surface area and lower mean pore diameter as

reported by Ghasemi *et al.* [152]. It is believed that in this case, surface area loss during high temperature calcination was inhibited due to the effect from metal incorporation.



ISOTHERM PLOT

Figure 4.21 Isotherm plot of 10wt%_9Cu1Ni_200_1

In terms of calcination temperature, the pore volume and pore diameter of photocatalyst increase as the temperature increase as shown in Table 4.3. However, the BET surface area reached the maximum (58 m²g⁻¹) for calcination at 200 °C. Meanwhile, for photocatalysts with different Cu:Ni mass composition, no such trend was found. As depicted in Table 4.4, the BET surface area of photocatalysts did not display any pattern as the copper content increased although the presence of metals increased the total surface area of bare TiO₂. High metal dispersion is contributed when the total surface area of photocatalysts increased.

In the case of photocatalytic activity, photocatalyst with the highest surface area (10wt%_5Cu5Ni_200_1) showed lower performance than other photocatalysts as displayed in Figure 4.4. This might be caused by the higher bandgap energy of 10wt% 5Cu5Ni 200 1 as can be seen in Table 4.2.

Higher bandgap energy leads to a lower activity of photocatalysts in terms of its capability to utilize photon energy from lower energy level (visible region). Therefore, it is suggested that surface area is not the main factor affecting the photocatalytic reaction as also observed by Quan and co-researcher [153] and Ranjit *et al.* [154].

Table 4.3 BET surface area, pore volume, and pore diameter of photocatalysts with different calcinations temperature

Photocatalyst	BET surface area	Total pore	Average pore
	(m^2g^{-1})	volume ($cm^{-3}g^{-1}$)	diameter (nm)
10wt%_5Cu5Ni_180_1	41	0.29	27.88
10wt%_5Cu5Ni_200_1	58	0.53	36.54
10wt%_5Cu5Ni_250_1	51	0.59	45.43

Table 4.4 BET surface area, pore volume, and pore diameter of photocatalysts with different Cu:Ni mass composition

Photocatalyst	BET surface area	Total pore	Average pore
	(m^2g^{-1})	volume (cm ⁻³ g ⁻¹)	diameter (nm)
10wt%_10Cu_200_1	47	0.25	21.22
10wt%_9Cu1Ni_200_1	43	0.27	24.85
10wt%_7Cu3Ni_200_1	46	0.40	35.01
10wt%_5Cu5Ni_200_1	58	0.53	36.54
10wt%_3Cu7Ni_200_1	46	0.35	29.95
10wt%_1Cu9Ni_200_1	44	0.32	28.58
10wt%_10Ni_200_1	48	0.37	30.49
Bare TiO ₂	43	0.20	18.46

The surface area of photocatalysts with different total metal loading are presented in Table 4.5. It is clearly seen that as the metal loading increased the overall surface area of photocatalyst slightly decreased. However, the pore size increased as the metal loading increased. Therefore, it may be concluded that the amount of metal loaded onto the surface of TiO_2 plays a significant role affecting the mesopore volume of photocatalyst. This is in good agreement with Millard and co-workers' [155] researching on Pd/TiO₂. On the other hand, different trend for Pt doped TiO₂ surface area was reported by Sreethawong and co-workers [125]. The effect of deposition of Pt on the outer and near the outer surface of the assembled TiO₂ particles result in the decrease in surface area and total pore volume, as the Pt loading increase, while the average pore diameter was found to remain unchanged.

Table 4.5 BET surface area, pore volume, and pore diameter of photocatalysts with different metal loading

Photocatalyst	BET surface area	Total pore volume	Average pore
	(m ² g ⁻¹)	(cm ⁻³ g ⁻¹)	diameter (nm)
5wt%_9Cu1Ni_200_1	43	0.27	24.45
10wt%_9Cu1Ni_200_1	43	0.27	24.85
15wt%_9Cu1Ni_200_1	40	0.29	28.85

The pore size distribution of 10wt%_5Cu5Ni_200_1 was calculated based on BJH desorption and the corresponding result is displayed in Figure 4.22. It is observed that the pore size distribution are well defined. The average pore diameter is 36.54 nm (365.4 Å), in a good agreement with the center of the maximum distribution at 200-300 Å. The pore size distribution also might explain the difference in the reduction (TPR) profiles of photocatalysts.



Figure 4.22 Pore size distribution of 10wt%_9Cu1Ni_200_1

As can be seen in Figure 4.23, the hydrogen consumption of the photocatalysts showed different peaks contributed to the presence of different metal particle size.

Generally, compared with bare TiO_2 , all doped photocatalysts have narrower pore size distribution as shown in Appendix D.

The average pore diameter of all photocatalysts showed the value between 210-360 Å, thus the photocatalysts can be categorized as mesopore catalyst (20 < d < 500 Å).

4.3.5 Temperature Programmed Reduction (TPR)

The TPR profiles of monometallic Cu/TiO₂, monometallic Ni/TiO₂ and bimetallic Cu-Ni/TiO₂ were presented in Figure 4.23. Temperature programmed reduction is used to characterize the photocatalysts in terms of their metal oxide species present, either copper oxide, nickel oxide, or copper-nickel mixed oxide, and the degree of interaction of the oxides with TiO₂ support.

It is clearly seen that for 10wt%_10Cu_200_1, two reduction peaks appeared at 205 °C and 256 °C. The small peak at 205 °C might be attributed to the reduction of highly dispersed CuO with less interaction with the TiO₂ support [92],[155]. Apparently, smaller CuO particles were formed on the surface of photocatalyst, decreasing the reduction temperature. On the other hand, the peak at higher temperature, 256 °C, was ascribed to the reduction of bulk CuO phase with stronger interaction with the TiO₂ support [92], [156]. Dow *et al.* [156] observed two reduction peaks of CuO in Al₂O₃, the small reduction peak around 200 °C might be due to the reduction of well dispersed copper oxide, which include isolated copper ions, weak magnetic associates, and small two- and three- dimensional clusters. As for the higher reduction peak at 280 °C was ascribed to bulk-like CuO phases that include large clusters and bulk CuO. Hence, the copper content, does not affect the reducibility of both copper oxide species. As the copper loading increase, the peak area does not shift.



Figure 4.23 TPR profiles of monometallic and bimetallic photocatalysts

The lower reduction temperature of CuO on CuO/CeO₂/TiO₂ was reported by Zhu *et al.* [156]. Three peaks appeared at 157 °C, 177 °C, and 257 °C. The peak at 157 °C may be related to the reduction of highly dispersed copper oxide species in close contact with the dispersed ceria on TiO₂ and reduction peak at 257 °C may be ascribed to the reduction of CuO cluster in contact with TiO₂. The TPR profile of monometallic Cu/TiO₂ was in good agreement with the results showed by the XRD and FESEM that the copper oxide was highly dispersed on TiO₂ photocatalyst.

The reduction profile of monometallic 10wt%_10Ni_200_1 displayed broad peak at 381 °C contributed to the reduction of NiO with strong interaction with TiO₂ [158]. The weaker shoulder peak detected at 286 °C corresponded to the well dispersed NiO with weak metal-support interaction [159].

The TPR profiles of bimetallic 10wt%_9Cu1Ni_200_1 showed two reduction peaks, 273 °C and 340 °C with a shoulder around 240 °C.

It is observed that the reduction peak and shoulder for CuO were shifted to higher temperature but on the other hand the reduction peak of NiO was shifted to lower temperature when compared with the monometallics Cu/TiO₂ and Ni/TiO₂. Reduction temperature for CuO was shifted from 205 °C to 240 °C and from 256 °C to 273 °C while reduction temperature for NiO was shifted from 381 °C to 340 °C. The distinct peak observed at 273 °C might be attributed to the reduction of Cu-Ni mixed oxide instead of individual oxide. The onset of reduction temperature was about 175 °C for the bimetallic photocatalyst compared to about 125 °C for Cu/TiO2. This may indicate the absence of individual CuO particle on the photocatalyst. The absence of the dominant peak at 381 °C (as observed for Ni/TiO₂) in the reduction profile of the bimetallic photocatalyst may also indicate the absence of individual NiO species. This result was in good agreement with that observed by Hernandez et al. [160] on Cu-Ni/ZrO2. It was found that the presence of Cu lowered the reduction temperature of Ni. Li et al. [69] observed the same behavior of bimetallic Cu-Ni/TiO₂. The addition of Cu enhanced the reduction of Ni, thereby it can be concluded that the reducibility of bimetallic Cu-Ni is controlled by the amount of Cu. However, the presence of CuO, NiO, as well as mixed CuO-NiO was not detected by XRD analysis due to welldispersed metal particle and well interaction of metal with TiO₂. TPR profiles of other photocatalysts with different Cu:Ni composition were displayed in Appendix E.

Photocatalyst	Reduction peak, °C	Amount of hydrogen
		adsorbed (µmol/g)
10wt%_10Cu_200_1	256	734
10wt%_9Cu1Ni_200_1	273, 340	1664
10wt%_7Cu3Ni_200_1	266	1938
10wt%_5Cu5Ni_200_1	179, 225, 314	1724
10wt%_3Cu7Ni_200_1	285	2048
10wt%_1Cu91Ni_200_1	222, 394, 639	2303
10wt%_10Ni_200_1	286, 381	2327

Table 4.6 Summary of the hydrogen consumption and the reduction temperature of the photocatalysts

4.3.6 X-ray Diffractrometer (XRD) of Photocatalysts

XRD pattern of photocatalysts with various copper to nickel mass composition are shown in Figure 4.24. As for comparison, bare TiO_2 is also displayed. It is obviously seen that bare TiO_2 as well as modified photocatalysts contain both anatase and rutile phases. The characteristic peaks at 20 of about 25.34°, 33.79°, 47.8°, 53.8° and 55.0° represent the crystalline structure of anatase [12], [13], [82], [91], [161]-[163] and the peak at 20 of about 27.40° correspond to the rutile phase of TiO_2 [88], [163].

It is also observed that there is no change in the crystalline phase of TiO_2 after calcination. This observation might be due to the low calcination temperature applied. The transition of anatase to the rutile phase occurs at temperature above 700 °C [16]. However, no characteristic reflection was found to indicate the presence of Ni, Cu, or their alloy containing phases in all photocatalysts which could indicate that metal particles are well dispersed or well interacted with TiO₂.



Figure 4.24 XRD patterns of a) bare TiO₂, b) 10wt%_10Cu_200_1, c) 10wt%_9Cu1Ni_200_1, and d) 10wt%_10Ni_200_1

This result was confirmed by FESEM image which showed high degree of metal dispersion. The use of glycerol in photocatalyst preparation favored the formation of small metal particle as it prevented the aggregation of metal particles [141]. XRD patterns of photocatalysts with different Cu:Ni mass composition and different total metal loading were presented in Appendix F.

Table 4.7 shows the particle size of photocatalysts calculated using Scherrer's equation (Equation 3.3). The calculation was done based on rutile and anatase phase. All the photocatalyst tend to have uniform particle size in the range of 20-40 nm, consistent with the particle size from FESEM images. Example of particle size calculation using Scherrer's equation was given in Appendix G.

Photocatalyst	Particle size, nm		
	Anatase	Rutile	
10wt%_10Cu_200_1	23.2	39.2	
10wt%_9Cu1Ni_200_1	20.1	38.6	
10wt%_7Cu3Ni_200_1	22.0	37.8	
10wt%_5Cu5Ni_200_1	20.2	31.2	
10wt%_3Cu7Ni_200_1	24.0	29.0	
10wt%_1Cu91Ni_200_1	21.8	37.8	
10wt%_10Ni_200_1	20.0	40.1	
TiO ₂	23.9	38.4	

Table 4.7 Particle size of the photocatalysts based on Scherrer's equation calculation

The composition of anatase and rutile phase in the photocatalysts was calculated based on the highest intensity of anatase and rutile (equation 3.4 and 3.5) and the corresponding results are displayed in Table 4.8.

Photocatalyst	Composition, %	
	Anatase	Rutile
10wt%_10Cu_200_1	82.15	17.85
10wt%_9Cu1Ni_200_1	80.96	19.04
10wt%_7Cu3Ni_200_1	83.23	16.77
10wt%_5Cu5Ni_200_1	84.45	15.55
10wt%_3Cu7Ni_200_1	85.42	14.58
10wt%_1Cu91Ni_200_1	84.52	15.48
10wt%_10Ni_200_1	80.71	19.29
TiO ₂	82.75	17.25

Table 4.8 Anatase and rutile composition in the photocatalysts

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, modification of TiO₂ has been carried out by adding Cu and Ni onto its surface using precipitation method in the presence of glycerol. The photocatalytic activities of the corresponding modified TiO₂ were investigated for hydrogen production from two different media: distilled water (H₂O) and mixture of distilled water and glycerol (H₂O+gly). Glycerol was added as sacrificial agent. The results clearly indicated that calcination condition applied for photocatalyst plays an important role for its photocatalytic activity. Research parameters such as calcination temperature, calcination duration, Cu:Ni mass composition, and total metal loading on the photocatalytic performance were evaluated. It was found that the optimum total loading was 10wt% with Cu:Ni mass composition of 9:1. The best pretreatment condition were observed for raw photocatalyst calcined at 200 °C for 1 h. This photocatalyst, 10wt%_9Cu1Ni_200_1, produced 6.1 mL H₂ in (H₂O) while in (H₂O+gly), the amount increased to 9.5 mL after 2 h of reaction.

The activity of photocatalyst for prolonged irradiation was also studied in two different media for 50 h. In the presence of glycerol (H₂O+gly), the photocatalyst showed better activity than that in distilled water (H₂O). The H₂ evolved was detected until 25 h reaction (20.2 mL) reaction for (H₂O+gly), while in (H₂O), the reaction stopped at 16 h (13.2 mL).

The addition of metal, both monometallic and bimetallic, onto the surface of TiO₂ has successfully modified the physical and chemical properties of bare TiO₂ which led to better photocatalytic performance. The absorption spectra was found to be shifted to the visible range thus reducing the bandgap energy of the photocatalyst. The lowest bandgap energy was 2.78 eV for 10wt%_9Cu1Ni_200_1, compared to 3.16 eV for bare TiO₂. The total surface area of the photocatalyst was also increased compared to that of bare TiO₂. Both surface area and bandgap energy of photocatalyst gives the synergetic effect for photocatalytic hydrogen production. High metal dispersion and small particle size also enhance the performance of modified TiO₂.

The intermediate products from glycerol oxidation were glycerldehyde, glycolic acid, and oxalic acid. These are value-added products from glycerol as they have many functions or industrial uses. It may be mentioned in this connection that glycerol is predicted to be a surplus byproduct of the bio-diesel production process and a clean route in its application as a sacrificial agent will serve the dual purpose of assisting in hydrogen generation as well as chemical production at no additional process step or cost [99], [111].

Kinetic study of photocatalytic hydrogen production from (H₂O) and (H₂O+gly) were studied as a function of photocatalyst concentration. The calculated apparent rate constant (k) and reaction order (n) for photocatalytic reaction from (H₂O) were 0.3195 $g^{0.84}$ L^{0.16} min⁻¹ and 0.160, respectively, while for photocatalytic reaction from (H₂O+gly) were 0.3989 $g^{0.805}$ L^{0.195} min⁻¹ and 0.195, repectively.

5.2 Recommendations

This study has proved that modification of TiO₂ with bimetallic Cu-Ni metal was effective for photocatalytic hydrogen production from water and water in the presence of glycerol. However, further studies are required in order to investigate the other parameters affecting the performance of bimetallic Cu-Ni/TiO₂. Preparation of photocatalyst with additional reduction step after calcination is recommended for further study. For a comparison study, different bare TiO₂ might be used.

 TiO_2 might be prepared by applying different method such as sol-gel method and microemulsion method. Thus the overall objective of future work should be to greatly improve the hydrogen production to make it competitive and also to identify the process conditions for selective chemical transformation of the sacrificial reagent to the target products.

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APPENDIX A

Calculation for Monometallic Cu/ TiO2 and Ni/ TiO2, and Bimetallic Cu-Ni/TiO2

1. Cu/TiO₂

Example for 10 g of 10 wt% Cu/TiO₂

To prepare, 100 g of catalyst 10 g of Cu was needed. Therefore, to prepare 10 g of photocatalyst, 1g of Cu was needed.

 $100 g of photocatalyst \rightarrow 10 g of Cu$ $10 g of photocatalyst \rightarrow 1 g of Cu$ $1mol of Cu(NO_3)_2.3H_2O \leftrightarrow 63.546 g of Cu$ $Molar mass of Cu(NO_3)_2.3H_2O = 241.60 g / mol$ $63.546 g Cu \leftrightarrow 241.60 g Cu(NO_3)_2.3H_2O$ $1g Cu = \frac{1 x 241.60}{63.546} = 3.8020 g Cu(NO_3)_2.3H_2O$

2. Ni/TiO₂

Example for 10 g of 10 wt% Ni/TiO₂

To prepare, 100 g of catalyst 10 g of metals were needed. Therefore, to prepare 10 g of photocatalyst, 1g of metal was needed.

100 g of photocatalyst →10 g of metal 10 g of photocatalyst →1 g of metal 1 mol of Ni(NO₃)₂.6H₂O ↔ 58.693 g of Ni Molar mass of Ni(NO₃)₂.6H₂O = 290.693 g / mol 58.693 g Ni ↔ 290.693 g Ni(NO₃)₂.6H₂O 1 g Ni = $\frac{1 \times 290.693}{58.693}$ = 4.9528 g Ni(NO₃)₂.6H₂O

3. Bimetallic Cu-Ni/TiO₂

Example for 10 g of 10 wt% 5Cu-5Ni/TiO₂ (mass composition of Cu:Ni=5:5) To prepare, 100 g of catalyst 10 g of metals were needed. Therefore, to prepare 10 g of photocatalyst, 1g of metal was needed

100 g of photocatalyst →10 g of metal 10 g of photocatalyst →1 g of metal 1 g of metal, mass composition of Cu : Ni = 5 : 5 → Cu = 0.5 g, Ni = 0.5 g 1 mol of Cu(NO₃)₂.3H₂O → 63.546 g of Cu 1 mol of Cu(NO₃)₂.3H₂O ↔ 63.546 g of Cu Molar mass of Cu(NO₃)₂.3H₂O = 241.60 g / mol 63.546 g Cu ↔ 241.60 g Cu(NO₃)₂.3H₂O 0.5 g Cu = $\frac{0.5 \times 241.60}{63.546}$ = 1.9010g Cu(NO₃)₂.3H₂O 1 mol of Ni(NO₃)₂.6H₂O ↔ 58.693 g of Ni Molar mass of Ni(NO₃)₂.6H₂O = 290.693 g / mol 58.693 g Ni ↔ 290.693 g Ni(NO₃)₂.6H₂O 0.5 g Ni = $\frac{1 \times 290.693}{58.693}$ = 2.4764 g Ni(NO₃)₂.6H₂O

APPENDIX B

Table B1. The amount of hydrogen evolved from all photocatalysts for photocatalytic hydrogen production in (H_2O) as reaction medium

	Photocatalyst	Calcination	Calcination	Cu:Ni mass	Total	H ₂
		temperature,	duration, h	composition	metal	evolved,
		°C			loading,	mL
					wt%	
M	10wt%_10Cu_200_1	200	1	10:0	10	5.0
	10wt%_10Ni_200_1	200	1	0:0	10	4.3
	5wt%_9Cu1Ni_200_1	200	1		5	3.0
	9wt%_9Cu1Ni_200_1	200	1		9	4.1
	10wt%_9Cu1Ni_200_1	200	1	9:1	10	6.1
	11wt%_9Cu1Ni_200_1	200	1	-	11	5.0
	15wt%_9Cu1Ni_200_1	200	1		15	4.9
	10wt%_7Cu3Ni_200_1	200	1	7:3	10	5.2
В	10wt%_5Cu5Ni_180_0.5		0.5		10	3.3
	10wt%_5Cu5Ni_180_1	180	1		10	4.4
	10wt%_5Cu5Ni_180_2		2		10	4.8
	10wt%_5Cu5Ni_200_0.5		0.5		10	3.3
	10wt%_5Cu5Ni_200_1	200	1		10	5.0
	10wt%_5Cu5Ni_200_2		2	5	10	5.0
	10wt%_5Cu5Ni_250_0.5		0.5		10	2.4
	10wt%_5Cu5Ni_250_1	250	1		10	4.4
	10wt%_5Cu5Ni_250_2		2		10	3.4
	10wt%_3Cu7Ni_200_1	200	1	3:7	10	2.4
	10wt%_1Cu9Ni_200_1	200	1	1:9	10	2.0
	TiO ₂	-	-	-	0	2.0

M = monometallic

 $\mathbf{B} = \text{bimetallic}$

APPENDIX C

[Bandgap Energy Estimation from DR-UV-Vis Spectra Results Using Tauc's Plot]



Figure C1. Tauc's plot for photocatalyst with different calcinations temperature



Figure C2. Tauc's plot for photocatalyst with different Cu:Ni mass composition



Figure C3. Tauc's plot for photocatalyst with different total metal loading

APPENDIX D

[SURFACE AREA ANALYSIS RESULTS]

ISOTHERM PLOT + ads, * des



Figure D1. Isotherm plot for TiO_2

dV/dlog(D) DESCRPTION PORE VOLUME PLOT







Figure D3. Isotherm plot for 10wt%_10Cu_200_1



Figure D4. Desorption pore volume plot for 10wt%_10Cu_200_1



Figure D5. Isotherm plot for 10wt%_7Cu3Ni_200_1

0.65 - 0.60 - 0.50 - 0.50 - 0.45 - 0.45 - 0.45 - 0.35 - 0.50 - 0.35 - 0.50 - 0.35 - 0.50 - 0.40 - 0.35 - 0.40 - 0.

PORE VOLUME , (cc/g)

0.30 0.25 0.20 0.15 0.10 0.20 0.05

10

3



PORE DIAMETER ,

1000

(A.)

100



Figure D7. Isotherm plot for 10wt%_5Cu5Ni_200_1



Figure D8. Desorption pore volume plot for 10wt%_5Cu5Ni_200_1

ISOTHERM PLOT



Figure D9. Isotherm plot for 10wt%_3Cu7Ni_200_1

105



Figure D10. Desorption pore volume plot for 10wt%_3Cu7Ni_200_1





Figure D11. Isotherm plot for 10wt%_1Cu9Ni_200_1

dv/dlog(D) DESORPTION PORE VOLUME PLOT



Figure D12. Desorption pore volume plot for 10wt%_1Cu9Ni_200_1



Figure D13. Isotherm plot for 10wt%_10Ni_200_1





Figure D14. Desorption pore volume plot for 10wt%_10Ni_200_1

ISOTHERM PLOT + ads, * des



Figure D15. Isotherm plot for 5wt%_9Cu1Ni_200_1





Figure D16. Desorption pore volume plot for 5wt%_9Cu1Ni_200_1





Figure D17. Isotherm plot for 15wt%_9Cu1Ni_200_1

dv/dlog(D) DESORPTION PORE VOLUME PLOT



Figure D18. Desorption pore volume plot for 15wt%_9Cu1Ni_200_1



Figure D19. Isotherm plot for 10wt%_5Cu5Ni_180_1



Figure D20. Desorption pore volume plot for 10wt%_5Cu5Ni_180_1



Figure D21. Isotherm plot for 10wt%_5Cu5Ni_250_1



Figure D22. Desorption pore volume plot for 10wt%_5Cu5Ni_250_1

APPENDIX E



Figure E1. TPR profile for 10wt%_10Cu_200_1



Figure E3. TPR profile for 10wt%_7Cu3Ni_200_1



Figure E4. TPR profile for 10wt%_5Cu5Ni_200_1



Figure E5. TPR profile for 10wt%_3Cu7Ni_200_1



Figure E6. TPR profile for 10wt%_1Cu9Ni_200_1



Figure E7. TPR profile for 10wt%_10Ni_200_1



Figure F1. XRD pattern for TiO₂



Figure F2. XRD pattern for 10wt%_10Cu_200_1



Figure F3. XRD pattern for 10wt%_9Cu1Ni_200_1







Figure F5. XRD pattern for 10wt%_5Cu5Ni_200_1



Figure F6. XRD pattern for 10wt%_3Cu7Ni_200_1



Figure F7. XRD pattern for 10wt%_1Cu9Ni_200_1



Figure F8. XRD pattern for 10wt%_10Ni_200_1



Figure F9. XRD pattern for 5wt%_9Cu1Ni_200_1



Figure F10. XRD pattern for 15wt%_9Cu1Ni_200_1

APPENDIX G

Particle size calculation using Scherrer's Equation

Particle size calculation for TiO₂:

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1. Particle size based on anatase phase was calculated for 2θ at 25.209° , FWHM = 0.351°

$$D = \frac{NR}{FWHM\cos\theta}$$

$$K = 0.9$$

$$\lambda = 1.54A$$

$$\theta = \frac{25.209^{\circ} \times 0.01745}{2} = 0.2199 \, radians$$

$$FWHM = 0.351^{\circ} \times 0.01745 = 0.0061 \, radians$$

$$D = \frac{0.9 \times 1.54}{0.0061 \, x\cos 0.2199}$$

$$D = 231.823A$$

$$D = 23.2 \, nm$$

2. Particle size based on rutilee phase was calculated for 2θ at 27.4° , FWHM = 0.166°

$$D = \frac{K\lambda}{FWHM\cos\theta}$$

K = 0.9
 $\lambda = 1.54A$
 $\theta = \frac{27.4^{\circ} \times 0.01745}{2} = 0.2301 radians$
FWHM = 0.166° x 0.01745 = 0.0029 radians
 $D = \frac{0.9 \times 1.54}{0.0613 \times \cos 0.2199}$
D = 492.3891A
D = 49.2 nm