

Solar Hydrogen from Glycerol-Water Mixture

Chong Fai Kait, Ela Nurlaela
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31750 Tronoh
Perak, Malaysia.

Binay K. Dutta
West Bengal Pollution Control Board
Paribesh Bhawan, Salt Lake
Kolkata 700 098, India.

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Abstract— The photocatalytic activity of titania supported bimetallic Cu-Ni photocatalysts were assessed for hydrogen production from water and also a mixture of glycerol-water system under visible light illumination. Addition of 2.0 mL glycerol to 8.0 mL water enhanced the solar hydrogen production from 6.1 mL to 9.5 mL. If metal was not incorporated onto TiO₂, the hydrogen production was minimal, 2.0 mL after 2 hr reaction. The band gap for bimetallic Cu-Ni/TiO₂ was 2.78 eV compared to 3.16 eV for TiO₂. Photooxidation of glycerol produced glyceraldehyde, glycolic acid and oxalic acid.

Keywords— Cu-Ni bimetallic; solar hydrogen; visible light; glycerol

I. INTRODUCTION

Hydrogen can be produced from various processes and the trend is moving from fossil fuels feedstock into renewable resources [1]. Solar hydrogen production from water offers an attractive and sustainable option since water is in abundance and the energy source from the sun is free. Titania, TiO₂ is the most popular photocatalyst used for solar hydrogen production [2]. However, due to its high band gap, the efficiency in visible light is low. The low efficiency of photohydrogen production is mainly due to the inability of TiO₂ to utilize visible light. The bandgap of TiO₂ is about 3.2 eV meaning that it can only be activated by photons with wavelength ≥ 400 nm (UV region). Since solar radiation consists of 3-4% UV component, visible light-active photocatalyst is a crucial requirement for economically feasible hydrogen production.

The low efficiency of photohydrogen production was also due to recombination reaction of photogenerated electrons and holes. Research on reducing the band gap has been vigorously conducted on water system by the incorporation of nonmetal [3] and metal components [4-5] and also with the addition of hole scavengers [6-7]. Some metals such as Cu, Ag, Au Ni, Rh, Pt and Zn were capable to increase the catalytic activity of the photocatalyst enhancing the hydrogen production [8-9]. Supported bimetallic catalysts have been widely used in industrial fields [10]. Bimetallic Cu-Ni has been reported to enhance carbon dioxide hydrogenation [11] and photocatalytic reduction of nitrates [12]. Hole scavengers are chemical species added into a photocatalytic system in order to stabilize the photogenerated holes, to prevent the electron-hole

recombination process. The hole scavengers undergo oxidation process. It would be beneficial if value-added products could be formed from the photoreaction.

Glycerol is a by-product from transesterification of fats and oils to produce biodiesel and also from the hydrolysis of palm oil (or other oils and fats) in soap and fatty acids manufacturing. This has caused an oversupply of glycerol. The photo-oxidation of glycerol was conducted using titania, TiO₂ [13-14] under the irradiation of UV light to produce useful chemicals such as dihydroxyacetone, glycolaldehyde, glyceraldehyde, formic acid and CO₂. Besides the production of glycerol derivatives, hydrogen has also been produced using TiO₂ doped with Pt [15], Au and Pd [16], Cu [17-19] and Ni [19]. However, the reactions were conducted under the irradiation of UV light.

In this study, bimetallic 10wt%Cu-Ni/TiO₂ and monometallic 10wt%Cu/TiO₂ and 10wt%Ni/TiO₂ photocatalysts were prepared, characterized and investigated for solar hydrogen production under visible light. It is expected that the activity region of the photocatalyst will be shifted to the visible light by metal doping. The addition of glycerol, which acts as hole scavenger will be able to enhance the hydrogen production efficiency. Products from the photooxidation process were also analyzed.

II. METHODOLOGY

A. Preparation of Cu-Ni/TiO₂ Photocatalyst

Degussa P25 TiO₂ was used as the support for all the photocatalysts. Bimetallic photocatalysts with 10wt% total metal loading were prepared via co-precipitation method to investigate the effect of Cu:Ni mass composition on solar hydrogen production efficiency. The monometallics 10wt% Cu/TiO₂ and 10wt% Ni/TiO₂ were also prepared in addition to TiO₂ as references. The metal precursors were copper(II) nitrate trihydrate (Acros, >98% purity) and nickel(II) nitrate hexahydrate (Acros, >98% purity). Glycerol (System, 95% purity) was used as a templating agent while sodium hydroxide, NaOH (Merck, 95%), was used as the precipitating agent. All the materials were used as received without further purification. Known amounts of Cu(NO₃)₂·3H₂O and/or Ni(NO₃)₂·6H₂O were weighed and dissolved in distilled water followed by the addition of glycerol. The solution was stirred continuously prior to addition of TiO₂. The slurry was stirred

for another hour before adding 0.25 M NaOH dropwise until pH = 12 to form precipitates. The mixture was aged for 1 day, filtered and dried overnight at 75°C in an oven. Calcination was conducted at 200°C for 1 hr. The effect of total metal loading on the performance for solar hydrogen production was also investigated. The drying and calcination temperatures and durations were selected based on previous study reported elsewhere [20].

B. Characterization of Cu-Ni/TiO₂ Photocatalyst

The bimetallic, monometallic and TiO₂ photocatalysts were characterized using powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and diffuse reflectance UV-Vis spectroscopy (DRUV-Vis).

The photocatalysts were analysed for the type of TiO₂ phases present using Bruker D8 Advance with CuK_α radiation (40 kV, 40 mA) at 2θ angles from 10° to 80°, with a scan speed of 4° min⁻¹. The morphology of the photocatalysts such as crystallite shape, size, and size distribution were analyzed using FESEM. The analyses were conducted using Zeiss Supra 35VP with 80 kX magnification and operating at 10 kV. DRUV-Vis measurement was performed using a Shimadzu Spectrometer 3150, equipped with an integrating sphere. BaSO₄ was employed as the reference material with analysis ranging from 190 to 800 nm. This technique is used to determine any shifting of the absorption edge to the visible region for the photocatalysts due to metal incorporation. The band gap energies of the photocatalysts could be determined from the Kubelka-Munk function, F(R), using the Tauc plot, a plot of (F(R).hv)^{1/2} against hv.

C. Solar Hydrogen Production

The photocatalysts were evaluated for solar hydrogen production using a multiport photocatalytic reactor integrated to water displacement units (Fig. 1) to monitor any gaseous product. A 500 W halogen lamp was used to simulate visible light, irradiating the photoreactor from the top giving an intensity of 12.2 klux.

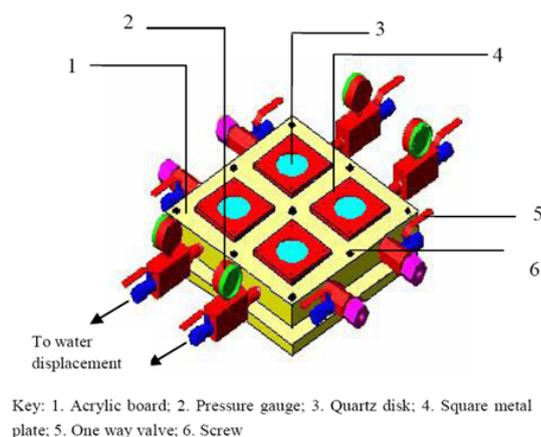


Fig. 1. Schematic of the multiport photocatalytic reactor

A 0.1 g of photocatalyst powder was suspended in distilled water (8.0 mL) and placed in the multiport reactor. The amount of gas evolved was monitored for 2 hr. The gaseous product

was analyzed using a gas chromatograph (Agilent 6890 series GC system) with 5A molecular sieve column (capillary 45.0 m × 530 μm × 25 μm) and equipped with thermal conductivity detector. Helium gas was used as the carrier gas.

For experiments where liquid glycerol was added as hole scavenger, the volume of glycerol was varied from 2.0 mL to 8.0 mL. Products from the photooxidation process were analyzed using high performance liquid chromatography (HPLC) (Agilent 1100 series) equipped with a Transgenomic column (ICE-ORH-801) and 0.01 N H₂SO₄ as eluent.

III. RESULTS AND DISCUSSION

A. Preparation of Cu-Ni/TiO₂ Photocatalyst

Bimetallic photocatalysts were prepared to investigate the effects of Cu:Ni mass composition, and total metal loading on the performance for solar hydrogen production. The 10 wt% monometallic photocatalysts were also prepared. Calcination was conducted at 200°C for 1 h duration. These pretreatment conditions were the optimum conditions selected based on previous work [20]. The photocatalysts were given denotation of 10wt%_9Cu1Ni for the bimetallic photocatalyst with 9:1 Cu:Ni mass composition while 10wt%_10Cu and 10wt%_10Ni were used for the monometallic Cu and Ni photocatalysts, respectively.

B. Characterization of Cu-Ni/TiO₂ Photocatalyst

Characterization procedures were conducted to determine the bulk and surface properties of the photocatalysts.

1) XRD

Fig. 2 shows the XRD patterns of the photocatalysts and TiO₂. The peaks were mainly characteristic peaks of the anatase phase at 2θ = 25.3°, 33.8°, 47.8°, 53.8° and 55.0°, while the rutile phase was represented by peaks at 2θ = 27.4° and 41.5°. It was found that no characteristic peaks representing Cu- or Ni-species could be detected indicating that the metal particles were well dispersed on TiO₂. The presence of glycerol during photocatalyst preparation contributed to the high metal dispersion [21-22]. The average crystallite size calculated using Scherrer equation was 35 nm.

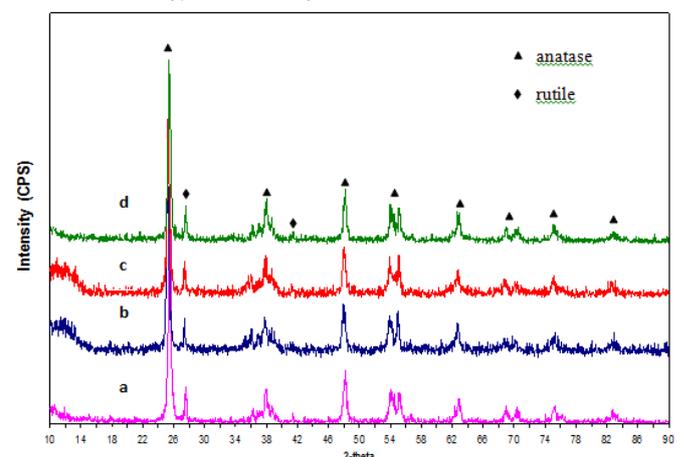


Fig. 2. XRD patterns of (a) TiO₂, (b) 10wt%_9Cu1Ni, (c) 10wt%_10Cu and (d) 10wt%_10Ni

2) FESEM

The FESEM images represented in Fig. 3 shows that the photocatalysts were present as uniform spherical shaped particles. All the photocatalysts tend to display slight agglomeration. The particle size of the photocatalysts ranged from 20-40 nm, in good agreement with the crystallite size calculated from the XRD data. However, no indication of localized metal deposition was observed, which was also confirmed by the XRD results – as the result of high metal dispersion [22].

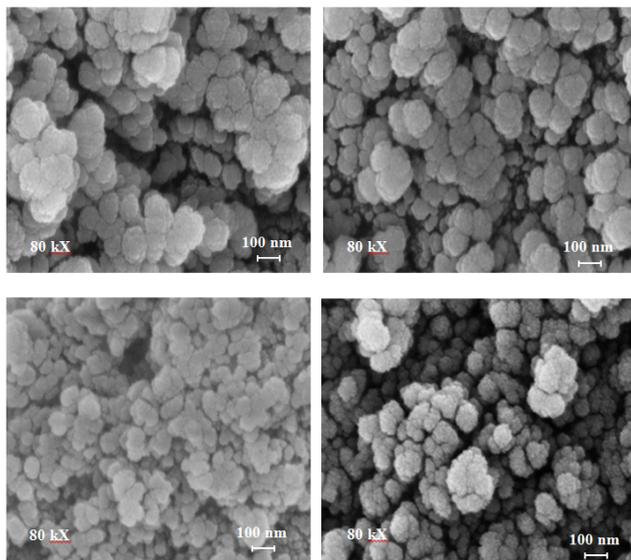


Fig. 3. FESEM images of (a) 10wt%_9Cu1Ni, (b) 10wt%_10Cu, (c) 10wt%_10Ni and (d) TiO₂

3) DRUV-Vis

DRUV-Vis spectrum of TiO₂ in Fig. 4 showed its absorption edge at 400 nm. No absorption was observed in the visible region. However, the edge shifted to the visible region with the addition of Cu, Ni or Cu-Ni indicating reduction in band gap values. Using Tauc plot (not shown), the band gaps were calculated and displayed in Table I. TiO₂ has the highest band gap of 3.16 eV. The addition of monometallic Cu or Ni reduced the band gap to 2.98 eV. Surface modification of TiO₂ with Cu, Ni or Cu-Ni could significantly reduce the band gap thus shifting the absorption edge to the visible region [23-25]. The lowest band gap was displayed by 10wt%_9Cu1Ni, 2.78 eV.

The presence of metal not only increased the visible light absorption, it also enhanced the absorbance in the UV region (wavelength <400 nm) as indicated by the higher absorbance of the bimetallic and monometallic photocatalysts compared to TiO₂ in Fig. 4. 10wt%_10Ni displayed the highest absorbance of approx. 0.19 followed by both 10wt%_10Cu and 10wt%_9Cu1Ni, and finally by TiO₂ displaying the lowest absorbance. The presence of Ni in 10wt%_9Cu1Ni seemed to enhance its visible light harvesting property. 10wt%_9Cu1Ni displayed the highest absorbance in the visible wavelength, and extending through to 800 nm. This was followed by 10wt%_10Cu and 10wt%_10Ni and finally TiO₂ displaying zero absorbance in the visible region.

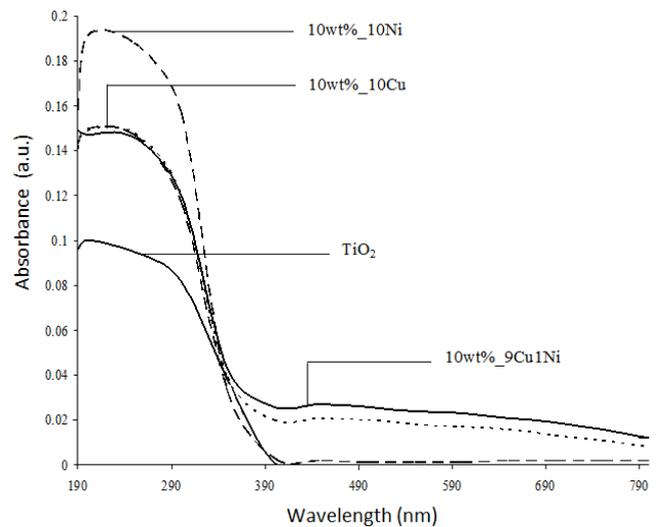


Fig. 4. DRUV-Vis spectra of the photocatalysts.

TABLE I. BAND GAP OF PHOTOCATALYSTS

Photocatalyst	Band gap, eV
TiO ₂	3.16
10wt%_10Cu	2.98
10wt%_9Cu1Ni	2.78
10wt%_7Cu3Ni	2.98
10wt%_10Ni	2.98

C. Solar Hydrogen Production

Referring to Fig. 5, the effect of Cu:Ni mass composition on the solar hydrogen production efficiency was investigated. Bimetallic 10wt%_9Cu1Ni photocatalyst displayed the highest hydrogen production of 6.1 mL compared to monometallic 10wt%_10Cu and 10wt%_10Ni, giving 5.0 mL and 4.3 mL, respectively. TiO₂ was able to produce only 2.0 mL gas. The reduction in band gap (Table I) for the photocatalysts compared to TiO₂ has led to an increase in hydrogen production from water.

The addition of a small amount of Ni onto Cu/TiO₂ (10wt%_9Cu1Ni) was able to enhance the performance of the photocatalyst from producing 5.0 mL to 6.1 mL hydrogen. This may be due to Cu acting as both hole and electron traps [26] while Ni as hole trap only [27]. However, as the composition of Ni increased (10wt%_7Cu3Ni), detrimental effect was observed resulting in lower amount of hydrogen produced. The increase in the amount of Ni led to it becoming the hole accumulation site which could attract the photogenerated electrons causing electron-hole recombination. During photoreaction, hydrogen should be produced together with oxygen. However, no oxygen was detected from the gas chromatography. This may be attributed to the oxygen itself acting as an electron acceptor leading to the formation of superoxide radical anions [28]. This may retard the continuous production of hydrogen causing the deactivation of the photocatalyst.

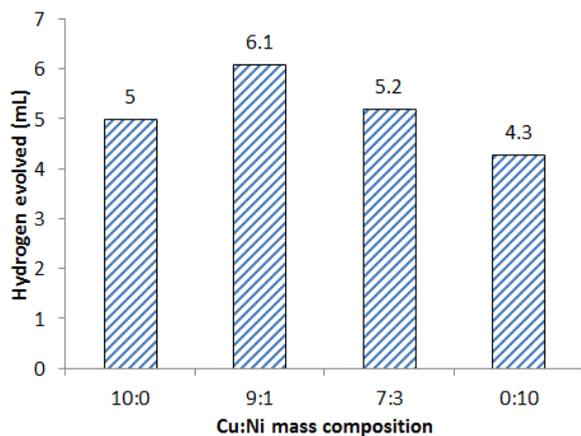


Fig. 5. The effect of Cu:Ni mass composition of photocatalyst with 10wt% total metal loading on hydrogen production.

Fig. 6 revealed that as the total metal loading of the photocatalysts (Cu:Ni mass composition of 9:1) was increased from 5 wt% to 10 wt%, the amount of hydrogen gas evolved increased from 3.0 mL to 6.1 mL. The presence of metal was able to inhibit the electron-hole recombination process [29]. However, when the total metal loading was increased to 11 wt%, the photocatalytic activity was reduced to 5.0 mL hydrogen evolved. Further increase in total metal loading showed lowered performance. As the total metal loading increases, the metal sites will act as electron-hole recombination centers due to electrostatic forces between the negatively charged metal sites and the positively charged holes [29-30]. The optimum loading for bimetallic Cu-Ni was 10wt%.

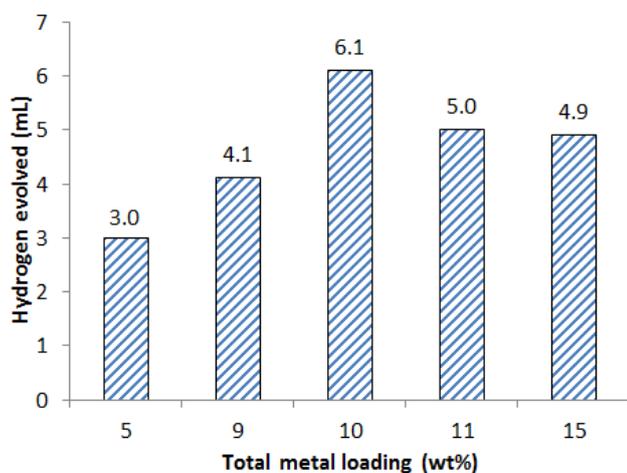


Fig. 6. The effect of total metal loading of photocatalyst (Cu:Ni mass composition 9:1) on hydrogen production.

From Fig. 7, the effect of glycerol amount on hydrogen production was investigated using 10wt% ₉Cu₁Ni. When 2.0 mL of glycerol was added, tremendous increase in the amount of hydrogen produced (9.5 mL) was observed. At this stage glycerol acts as a hole scavenger [18] diminishing the effect of electron-hole recombination. Although the amount of hydrogen produced decreased when more glycerol was added, the overall effect was enhancement of performance compared to without

glycerol addition. The decreased performance with higher amount of glycerol may be due to the competitive adsorption of glycerol, its intermediates and water onto the photocatalyst surface [31].

The intermediate products identified from glycerol photooxidation were glyceraldehyde, glycolic acid, and oxalic acid. The use of glycerol as sacrificial agent for hydrogen production from water serves not only to enhance the photocatalytic performance but also the generation of value-added products from the biodiesel by-product.

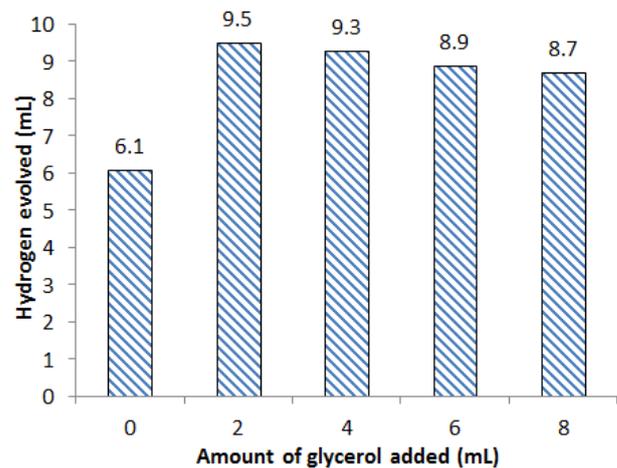


Fig. 7. The effect of glycerol amount on hydrogen production using 10wt% ₉Cu₁Ni.

IV. CONCLUSION

The photocatalysts displayed high metal dispersion. Particles were spherical shaped with slight agglomeration with size ranging from 20-40 nm. The addition of Cu, Ni or bimetallic Cu-Ni onto TiO₂ led to reduction in band gap from 3.16 eV to 2.78 eV for 10wt% ₉Cu₁Ni photocatalyst. This led to enhancement in the hydrogen production (6.1 mL) under visible light illumination compared to TiO₂. The addition of 2.0 mL of glycerol as hole scavenger further enhanced the solar hydrogen production to 9.5 mL. The photooxidation of glycerol under visible light illumination produced glyceraldehyde, glycolic acid and oxalic acid.

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REFERENCES

- [1] M. Momirlan, and T. Vezirog, "Recent directions of world hydrogen production", *Renewable and sustainable energy reviews*, vol. 3, pp. 219-231, 1999.
- [2] M. Ni, M.K.H. Leung, D.Y.C., and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production", *J. Renewable and Sustainable Energy Reviews*, vol. 11, pp 401-425, 2007.

- [3] M. Kitano, M. Matsuoka, M. Ueshima, and M. Anpo, "Recent developments in titanium oxide-based photocatalysts", *Applied Catalysis A: General* vol. 325, pp.1-14, 2007.
- [4] A. Kudo, R. Niishiro, A. Iwase, H. Kato, "Effects of doping of metal cations on morphology, activity, and visible light response of photocatalysts", *Chemical Physics*, vol 339, pp.104-110, 2007.
- [5] J.P. Yasomanee, and J. Bandara, "Multi-electron storage of photoenergy using Cu₂O-TiO₂ thin film photocatalyst", *Solar Energy Materials and Solar Cells*, vol. 92, pp.348-352, 2008.
- [6] J. Premkumar, "Development of Super-Hydrophilicity on Nitrogen-Doped TiO₂ Thin Film Surface by Photoelectrochemical Method under Visible Light", *Chemistry Materials*, vol. 16, pp.3980-3981, 2004.
- [7] J. Bandara, C.P.K. Udawatta, and C.S.K. Rajapakse, "Highly stable CuO incorporated TiO₂ catalyst for photocatalytic hydrogen production from H₂O", *Journal of Photochemistry and Photobiological Science*, vol. 4, no. 11, pp. 857-861, 2005.
- [8] G.L. Chiarello, E. Selli, L. Forni, "Photocatalytic Hydrogen Production Over Flame Spray Pyrolysis-synthesised TiO₂ and Au/TiO₂", *Applied Catalysis B: Environmental*, vol. 84, pp. 332-342, 2008.
- [9] Z.M. El-Bahy, A.A. Ismail, R.M. Mohamed, "Enhancement of Titania by Doping Rare Earth for Photodegradation of Organic Dye (Direct Blue)", *Journal of Hazardous Materials*, vol. 166, no.1, pp. 138-143, 2008.
- [10] V. Ponec, "Alloy catalysts: the concepts", *Applied Catalysis A: General*, vol. 222, pp. 31-45, 2001.
- [11] Y. Liu, D. Liu, "Study of Bimetallic Cu-Ni/Al₂O₃ Catalysts for Carbondioxide Hydrogenation", *Int. Journal of Hydrogen Energy*, vol. 24, pp. 351-354, 1999.
- [12] W.Gao, R. Jin, J. Chen, X. Guang, H. Zheng, F. Zhang, N. Guan, "Titania-supported Bimetallic Catalysts for Photocatalytic Reduction of Nitrate", *Catalysis Today*, vol. 90, pp. 331-336, 2004.
- [13] V. Maurino, A. Bedini, M. Minella, F. Rubertelli, E. Pelizzetti, and C. Minero, "Glycerol Transformation Through Photocatalysis: A Possible Route to Value Added Chemicals", *Journal of Advanced Oxidation Technologies*, vol. 11, no. 2, pp. 184-192, 2008.
- [14] V. Augugliaro, H.A. Hamed El Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano, and S. Yurdakal, "Partial photocatalytic oxidation of glycerol in TiO₂ water suspensions", *Catalysis Today*, vol. 151, no. 1-2, pp. 21-28, 2010.
- [15] M. Li, Y. Li, S. Peng, G. Lu, and S.B. Li, 2009, "Photocatalytic hydrogen generation using glycerol wastewater over Pt/TiO₂", *Frontiers of Chemistry in China*, vol. 4, no.1, pp. :32-38, 2009.
- [16] M. Bowker, P.R. Davies, and L.S. Al-Mazroai, "Photocatalytic Reforming of Glycerol over Gold and Palladium as an Alternative Fuel Source", *Catal Lett*, vol. 128, pp. 253-255, 2009.
- [17] G. Li, N.M. Dimitrijevic, L. Chen, T. Rajh, and K.A. Gray, "Role of Surface/Interfacial Cu²⁺ Sites in the Photocatalytic Activity of Coupled CuO-TiO₂ Nanocomposites", *J. Phys. Chem, C*, vol. 112, pp. 19040-19044, 2008.
- [18] V. Gombac, L. Sordelli, T. Montini, J.J. Delgado, A. Adamski, G. Adami, M. Cargnello, S. Bernal, and P. Fornasiero, "CuO_x-TiO₂ Photocatalysts for H₂ Production from Ethanol and Glycerol Solutions", *J. Phys. Chem, A*, vol. 114, pp. 3916-3925, 2010.
- [19] A.V. Korzhak, N.I. Ermokhina, A.L. Stroyuk, V.K. Bukhtiyarov, A.E. Raevskaya, V.I. Litvin, S.Y. Kuchmiy, V.G. Ilyin, and P.A. Manorik, "Photocatalytic hydrogen evolution over mesoporous TiO₂/metal nanocomposites", *Journal of Photochemistry and Photobiology A: Chemistry*, vol.198, no. 2-3, pp. 126-134, 2008.
- [20] Ela Nurlaela, "Development of Cu-Ni/TiO₂ bimetallic catalyst for photohydrogen production under visible light illumination", M.Sc. Thesis, Universiti Teknologi PETRONAS, 2011.
- [21] Y. Li, M. Cai, J. Rogers, Y. Xu, and W. Shen, "Glycerol-mediated synthesis of Ni and Ni/NiO core-shell nanoparticles," *Materials Letters*, vol. 60, pp. 750-753, 2006.
- [22] L.S. Yoong, F.K. Chong, and B.K. Dutta, "Development of copper-doped TiO₂ photocatalyst for hydrogen production under visible light " *Energy*, vol. 34, pp. 1652-1661, 2009.
- [23] J. Escobar, J. A. D. L. Reyes, and T. Viveros, "Nickel on TiO₂-modified Al₂O₃ sol-gel oxides: Effect of synthesis parameters on the supported phase properties," *Applied Catalysis A*, vol. 253, pp. 151-163, 2004.
- [24] O. V. Komova, A. V. Simakov, V. A. Rogov, D. I. Kochubei, G. V. Odegova, V. V. Kriventsov, E. A. Paukshtis, V. A. Ushakov, N. N. Sazonova, and T. A. Nikoro, "Investigation of the state of copper in supported copper-titanium oxide catalysts," *Journal of Molecular Catalysis A*, vol. 161, pp. 191-204, 2000.
- [25] T. Umabayashi, T. Yamaki, H. Itoh, K. Asai, "Analysis of electronic structures of 3d transition metal-dope TiO₂ based on band calculation", *Journal of Physics and Chemistry Solids*, vol. 63, pp. 1909-1920, 2002.
- [26] T. Miwa, S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, S.C. Verma, and K. Sugihara, "Photocatalytic hydrogen production from aqueous methanol solution with CuO/Al₂O₃/TiO₂ nanocomposite," *International Journal of Hydrogen Energy*, vol. 35, pp. 6554-6560, 2010.
- [27] D. Jing, L. Guo, L. Zhao, "Study on the synthesis of Ni doped mesoporous TiO₂ and its photocatalytic activity for hydrogen evolution in aqueous methanol solution," *Chemical Physics Letters*, vol.415, pp. 74-78, 2005.
- [28] D.H. Tseng, L.C. Juang and H.H. Huang, "Effect of oxygen and hydrogen peroxide on the photocatalytic degradation of monochlorobenzene in TiO₂ aqueous suspension", *International Journal of Photoenergy*, vol. 2012, pp. 1-9, 2012.
- [29] O. Carp, C. L. Huisman, and A. Reller, "Photoinduced Reactivity of Titanium Dioxide", *Progress in Solid State Chemistry*, vol. 32, pp. 33-117, 2004.
- [30] T. Sreethawong, S. Laehsabee, and S. Chavadej, "Use of Pt/N-doped mesoporous-assembled nanocrystalline TiO₂ for photocatalytic H₂ production under visible light irradiation", *Catalysis Communications*, vol. 10, pp. 538-543, 2009.
- [31] S. Chavadej, P. Phuaphromyod, E. Gulari, P. Rangsunvigit, and T. Sreethawong, "Photocatalytic degradation of 2-propanol by using Pt/TiO₂ prepared by microemulsion technique," *Chemical Engineering Journal*, vol. 137, pp. 489-495, 2008.

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