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 TiO$_2$, the hydrogen production was minimal, 2.0 mL after 2 hr reaction. The band gap for bimetallic Cu-Ni/TiO$_2$ was 2.78 eV compared to 3.16 eV for TiO$_2$. 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, TiO$_2$ 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 TiO$_2$ to utilize visible light. The band gap of TiO$_2$ is about 3.2 eV meaning that it can only be activated by photons with wavelength $\geq$ 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 reaction. 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, TiO$_2$ [13-14] under the irradiation of UV light to produce useful chemicals such as dihydroxyacetone, glycolaldehyde, glyceraldehyde, formic acid and CO$_2$. Besides the production of glycerol derivatives, hydrogen has also been produced using TiO$_2$ 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/TiO$_2$ and monometallic 10wt%Cu/TiO$_2$ and 10wt%Ni/TiO$_2$ 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/TiO$_2$ Photocatalyst

Degussa P25 TiO$_2$ 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/TiO$_2$ and 10wt% Ni/TiO$_2$ were also prepared in addition to TiO$_2$ 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(NO$_3$)$_2$.3H$_2$O and/or Ni(NO$_3$)$_2$.6H$_2$O were weighed and dissolved in distilled water followed by the addition of glycerol. The solution was stirred continuously prior to addition of TiO$_2$. 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/TiO$_2$ Photocatalyst

The bimetallic, monometallic and TiO$_2$ 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 TiO$_2$ phases present using Bruker D8 Advance with CuK$_{alpha}$ radiation (40 kV, 40 mA) at 20 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. BaSO$_4$ 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).h$^2$) against h$^2$.

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.

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 Transgenic column (ICE-ORH-801) and 0.01 N H$_2$SO$_4$ as eluent.

III. RESULTS AND DISCUSSION

A. Preparation of Cu-Ni/TiO$_2$ 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 hr 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/TiO$_2$ 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 TiO$_2$. The peaks were mainly characteristic peaks of the anatase phase at 20 = 25.3°, 33.8°, 47.8°, 53.8° and 55.0°, while the rutile phase was represented by peaks at 20 = 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 TiO$_2$. 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. 1. Schematic of the multiport photocatalytic reactor

Fig. 2. XRD patterns of (a) TiO$_2$, (b) 10wt%_9Cu1Ni, (c) 10wt%_10Cu and (d) 10wt%_10Ni

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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) TiO\(_2\)].

3) **DRUV-Vis**

DRUV-Vis spectrum of TiO\(_2\) 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. TiO\(_2\) 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 TiO\(_2\) 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.

![Fig. 4. DRUV-Vis spectra of the photocatalysts.]

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 TiO\(_2\) in Fig. 4. 10wt%_10Ni displayed the highest absorbance of approx. 0.19 followed by both 10wt%_10Cu and 10wt%_9Cu1Ni, and finally by TiO\(_2\) 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 TiO\(_2\) displaying zero absorbance in the visible region.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Band gap, eV</th>
</tr>
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<tbody>
<tr>
<td>TiO(_2)</td>
<td>3.16</td>
</tr>
<tr>
<td>10wt%_10Cu</td>
<td>2.98</td>
</tr>
<tr>
<td>10wt%_9Cu1Ni</td>
<td>2.78</td>
</tr>
<tr>
<td>10wt%_7Cu3Ni</td>
<td>2.98</td>
</tr>
<tr>
<td>10wt%_10Ni</td>
<td>2.98</td>
</tr>
</tbody>
</table>

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. TiO\(_2\) was able to produce only 2.0 mL gas. The reduction in band gap (Table I) for the photocatalysts compared to TiO\(_2\) has led to an increase in hydrogen production from water.

The addition of a small amount of Ni onto Cu/TiO\(_2\) (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 10 wt% 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 10 wt%.

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

From Fig. 7, the effect of glycerol amount on hydrogen production was investigated using 10 wt% 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.

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 10 wt% 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


