Simulation of Solar Hydrogen Production from Water in the Presence of TiO$_2$-Supported Bimetallic Cu-Ni Photocatalyst

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Abstract: Titania-supported monometallic and bimetallic Cu, Ni and Cu-Ni photocatalysts were prepared, characterized and assessed for hydrogen production from water under visible light illumination. The bimetallic photocatalyst displayed the best hydrogen production (6.1 mL) compared to titania (2.0 mL). The monometallic Cu/TiO$ _2$ and Ni/TiO$_2$ were less reactive producing 5.0 mL and 4.3 mL hydrogen gas, respectively. The presence of bimetallic Cu-Ni reduced the photocatalyst band gap to 2.78 eV compared to 3.16 eV for TiO$_2$. The experimental data was used to get the mathematical models, so that the hydrogen production system can be simulated by using actual solar insolation data.

Key words: Copper • Copper-nickel • Nickel • Solar hydrogen

INTRODUCTION

The world is shifting its focus from fossil fuel to renewable energy for sustainability [1]. Since water and sunlight are resources that are in abundance and free, it would be ideal to utilize them for solar hydrogen production. Titania, (TiO$_2$) is widely used as a photocatalyst especially for solar hydrogen production [2]. However, it displays low efficiency due to its high band gap (3.2 eV) and also the high rate of electron-hole recombination. Therefore, TiO$_2$ is only active in the UV region of the electromagnetic spectrum. In order for the photocatalyst to harvest the energy from the sun more efficiently, the activity region of the photocatalyst needs to be shifted to the visible region.

Modification of TiO$_2$ by metal doping [3-8] has been proven to increase its activity under visible light. Metals such as Cu, Ag, Au, Ni, Rh, Pt and Zn were capable to increase the catalytic activity for hydrogen production [9,10]. The electron-holes recombination could be reduced in the presence of these metals resulting in more efficient photocatalytic performance. In addition to metal incorporation, research was also conducted to study the effect of the presence of hole scavengers on the photoactivity [11, 12]. In the presence of Cu [13-15] and Ni [15], hydrogen was also produced simultaneously under the irradiation of UV light.

In this study, 10wt% bimetallic Cu-Ni and 10wt% monometallic Cu and Ni photocatalysts were prepared, characterized and investigated for solar hydrogen production under visible light. It is expected that the addition of Cu or/and Ni metals will be able to enhance the hydrogen production efficiency under visible light.

MATERIALS AND METHODS

Preparation of Photocatalyst: Monometallic and bimetallic photocatalysts with total metal loading of 10wt% were prepared via co-precipitation method. Degussa P25 TiO$_2$ was used as the support. For the 10wt% Cu-Ni/TiO$_2$ bimetallic photocatalyst, the Cu:Ni mass composition was 9:1. The Cu:Ni mass composition, calcination temperature and duration were selected based on previous study reported elsewhere [16]. The metal precursors used were copper(II) nitrate trihydrate (Acros, >98% purity) and nickel(II) nitrate hexahydrate (Acros, >98% purity) with water as solvent. Glycerol (Systerm, 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. After the precipitation process at pH 12, the mixture was aged for 1 day prior to filtering and drying in an oven overnight at 75°C. Calcination was conducted at 200°C for 1 hr.

The photocatalysts were given denotation of Cu-Ni for the 10wt% bimetallic photocatalyst with 9:1 Cu:Ni mass composition while Cu and Ni were used for the 10 wt% monometallic Cu and Ni photocatalysts, respectively.

**Characterization of Photocatalyst:** The photocatalysts were characterized using powder X-ray diffraction (XRD) and diffuse reflectance UV-Vis spectroscopy (DRUV-Vis).

The photocatalysts were analysed by using Bruker D8 Advance XRD with CuKα radiation (40 kV, 40 mA) at 2θ angles from 10° to 80°, with a scan speed of 4°•min⁻¹. DRUV-Vis measurement was conducted on the photocatalysts using a Shimadzu Spectrometer 3150, equipped with an integrating sphere and BaSO₄ was employed as the reference material. Spectra were recorded with wavelength 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).hν)² against hν.

**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.

Distilled water was the reaction medium for all photocatalysis. A 0.1 g of photocatalyst powder was suspended in 8.0 mL of distilled water and placed in the multiport photoreactor. 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 im) and equipped with thermal conductivity detector. Helium gas was used as the carrier gas.

The process flow for the solar hydrogen production is given in Fig. 2, where it can be seen that there is a need to analyze the amount of possible solar insolation that can be received by the photoreactor. The simulations were carried out by using fixed halogen lamp with constant irradiance. In reality, the solar insolation is not constant and the intensity varies due to the apparent trajectory of the sun and meteorological conditions, as shown in Fig. 3.

The solar insolation, \( I \) in W/m², shown in Fig. 3 can be represented by a polynomial curve fit expression, as given by Equation (1), where \( t \) is time in min between 0830h and 1900h and the correlation factor is 97.8%. 

![Fig. 1: Schematic of the multiport photocatalytic reactor](image1)

![Fig. 2: Process flow for hydrogen production](image2)

![Fig. 3: The measured daily average solar insolation](image3)
Equation (1) will be useful to simulate the experimental outcomes that were obtained by using halogen lamp, as the actual solar insolation is transient in nature [17].

\[ I_G = 49.1 + 7.05r - 0.0198r^2 + 2.9 \times 10^{-5}r^3 - 2.4 \times 10^{-8}r^4 \] (1)

RESULTS AND DISCUSSION

Characterization of Cu-Ni/TiO\(_2\) Photocatalyst

XRD: Fig. 4 shows the XRD patterns of the photocatalysts. The peaks were mainly characteristic peaks of the anatase phase of TiO\(_2\) at 2\(\theta\) = 25.3°, 33.8°, 47.8°, 53.8° and 55.0°, while the rutile phase was represented by peaks at 2\(\theta\) = 27.4° and 41.5°. It was found that no characteristic peaks representing Cu, Ni, or Cu-Ni species could be identified which indicated well dispersed metal particles on TiO\(_2\). This may be attributed to the presence of glycerol during photocatalyst preparation which contributed to the high metal dispersion [18, 19]. The average crystallite size calculated using Scherrer equation was 35 nm.

DRUV-Vis: DRUV-Vis spectrum of TiO\(_2\) in Fig. 5 showed its absorption edge at 400 nm. The presence of metal not only increased the visible light absorption, but also enhanced the absorption in the UV region. Cu-Ni displayed the highest absorption in the visible region, extending through to 800 nm. The extension of the absorption edge to the visible region indicated reduction in band gap.

The band gaps were calculated and displayed in TABLE I. TiO\(_2\) has the highest band gap of 3.16 eV. 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 [20-22].

Solar Hydrogen Production: The volume of hydrogen gas produced achieved steady state after 80 min of reaction. Referring to Fig. 6, bimetallic Cu-Ni photocatalyst displayed the highest hydrogen production of 6.1 mL compared to monometallic Cu and Ni, giving 5.0 mL and 4.3 mL, respectively. The addition of a small amount of Ni to Cu/TiO\(_2\) (Ni:Cu 1:9 mass composition) enhanced the performance of the photocatalyst. This may be due to Cu acting as both hole and electron traps [23] while Ni as hole traps only [24]. The photocatalyst performance was

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Band gap, eV</th>
<th>Volume H(_2) evolved, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>3.16</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>2.98</td>
<td>4.3</td>
</tr>
<tr>
<td>Cu</td>
<td>2.98</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>2.78</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Fig. 7: The estimated daily solar hydrogen production by using different photocatalysts.

Table II: Value of Coefficients (C) Deduced from Equation (2) and Figure 6.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>C(mL/MJm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.6715</td>
</tr>
<tr>
<td>Ni</td>
<td>1.4438</td>
</tr>
<tr>
<td>Cu</td>
<td>1.6788</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>2.0482</td>
</tr>
</tbody>
</table>

in agreement with the band gap tabulated in TABLE I in which the best performing Cu-Ni photocatalyst has the lowest band gap of 2.78 eV.

The linear simulation models were obtained for the volume of hydrogen produced by using the photocatalysts as shown in Fig. 6. The general linear equation is given in Equation (2) and the coefficients C for different photocatalysts are given in TABLE II.

\[ V_H = kCI_0 \]  

(2)

where

- \( V_H \) = Volume of \( H_2 \) produced (mL)
- \( k \) = Conversion factor (3.6 × 10⁻⁳ MJ/W)
- \( C \) = Photocatalyst coefficient (mL/MJm⁻²)
- \( I_0 \) = Solar insolation (W/m²)

These models were then employed to estimate the amount of solar hydrogen that can be produced when subjected to actual outdoor conditions, as shown in Fig. 3. Fig. 7 shows the estimated daily production of solar hydrogen, \( V_H \) in mL when subjected to actual outdoor conditions. Based on the plot for best performing Cu-Ni photocatalyst and also Equation (2), under the actual solar insolation the average hydrogen production per hour was 4.89 mL·h⁻¹. The amount of solar hydrogen produced for a 10-h exposure to actual solar insolation would produce a total of 48.90 mL in a day.

CONCLUSION

The photocatalysts displayed better performance with the addition of Cu, Ni or bimetallic Cu-Ni onto TiO₂. The highest reduction in band gap from 3.16 eV to 2.78 eV for the bimetallic photocatalyst was also observed. The modification with metal led to the enhancement in the hydrogen production under visible light illumination compared to bare TiO₂. The simulations by using actual outdoor solar insolation data showed that the daily productions are at 69% of the standard testing values. Hence, the production of solar hydrogen from water is feasible with the use of bimetallic Cu-Ni photocatalyst.

ACKNOWLEDGMENT

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REFERENCES


