Journal of
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Photocatalytic Biohydrogen Production Using ZnO from Aqueous Glycerol Solution with Aid of Simultaneous Cu Deposition

Mahmudul Hassan Suhag [1,2,*], Ikki Tateishi [3], Mai Furukawa [1], Hideyuki Katsumata [1], Aklima Khatun [1] and Satoshi Kaneco [1,*]

[1] Department of Applied Chemistry, Graduate School of Engineering, Mie University, Tsu 514-8507, Mie, Japan; maif@chem.mie-u.ac.jp (M.F.); hidek@chem.mie-u.ac.jp (H.K.); aklimarowsan_sust@yahoo.com (A.K.)
[2] Department of Chemistry, University of Barishal, Barishal 8254, Bangladesh
[3] Mie Global Environment Center for Education & Research, Mie University, Tsu 514-8507, Mie, Japan; tateishi@gecer.mie-u.ac.jp
* Correspondence: suhag.che057@gmail.com (M.H.S.); kaneco@chem.mie-u.ac.jp (S.K.); Tel.: +81-59-231-9427 (M.H.S. & S.K.)

Abstract: Biodiesel has gained a great deal of attention as a new sustainable energy alternative to petroleum-based fuels. The subsequent increased biodiesel production requires new utilization of glycerol, which is a byproduct of biodiesel synthesis. Photocatalytic biohydrogen generation using ZnO with the aid of simultaneous deposition of copper from an aqueous biomass-derivative glycerol solution was investigated. The effects of the concentration of glycerol solution, Cu ion concentration, and reaction temperature on biohydrogen generation were investigated. The photocatalytic biohydrogen production rate increased as the concentration of aqueous glycerol solution increased, and the observed data could be fitted to the Langmuire–Hinshelwood kinetic models. The photocatalytic H_2 production efficiency with ZnO could be significantly improved by simultaneous Cu deposition. The photocatalytic biohydrogen production rate was dependent on temperature, and increased as the temperature increased. Under the optimal conditions, the photocatalytic H_2 production rate was 72 µmol h^{-1} g^{-1} from the aqueous biomass-derivative glycerol solution. Possible mechanisms for the oxidation of glycerol solution and photocatalytic hydrogen generation were proposed.

Keywords: photocatalytic biohydrogen production; photocatalyst; glycerol solution; simultaneous Cu deposition; ZnO

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Citation: Suhag, M.H.; Tateishi, I.; Furukawa, M.; Katsumata, H.; Khatun, A.; Kaneco, S. Photocatalytic Biohydrogen Production Using ZnO from Aqueous Glycerol Solution with Aid of Simultaneous Cu Deposition. *J. Compos. Sci.* **2023**, *7*, 361. https://doi.org/10.3390/jcs7090361

Academic Editor: Francesco Tornabene

Received: 11 August 2023
Accepted: 26 August 2023
Published: 29 August 2023

1. Introduction

The demand for environmentally friendly, sustainable, and renewable energy resources has gradually increased due to the excessive depletion of fossil fuel resources, environmental pollution, and global warming [1,2]. In the near future, hydrogen (H_2) is expected to become an important renewable energy resource because of its unique eco-friendly and renovation properties [3].

The uses of biomass derivatives such as alcohols, sugars, glycerol, and glucose in hydrogen production are very interesting and significant for the effective recycling of materials [4–7]. Among biomass derivatives, glycerol can be produced in large amounts as a byproduct of the vegetable oil transformation in the biodiesel fuels, soap manufacture, and lignocellulose-to-ethanol conversion industries [8]. The produced crude glycerol can be utilized in the H_2 generation process via partial oxidation, aqueous phase reforming, steam reforming, autothermal reforming, supercritical water reforming methods, and photocatalytic splitting [9–14]. Therefore, glycerol is a storable, reasonable, and environmentally friendly compound which can be used in the generation of hydrogen energy from biomass derivatives.

One of the potential sustainable methods for transforming solar energy into chemical energy is photocatalytic hydrogen generation. Photocatalytic H_2 production from glycerol can be environmentally responsive and cost effective. Hence, photocatalytic H_2 production from glycerol is an attractive choice, owing to its lower-energy-consuming features compared to other methods [15]. Moreover, only photocatalysts and sunlight are essential for the photocatalytic reaction under ambient conditions [6]. Nowadays, metal oxides such as ZnO and TiO_2 have received a lot of attention and have been identified as effective photocatalysts for hydrogen production because of their eco-friendly, low-cost, high photo stability, and chemical stability properties [16,17]. The lower photoactivities of ZnO and TiO_2 are the main limitations regarding their use in photocatalytic H_2 production. The large band gap, rapid electron hole pair recombination rate during irradiation of light, and existence of reverse reactions are responsible for their lower photo activity in hydrogen production reactions [1,18]. Many strategies, such as doping and the formation of composites with another semiconductor or metal nanoparticles, have been adopted to reduce the rate of electron hole pair recombination and the energy radiation band gap and to improve the photocatalytic H_2 generation performance of ZnO and TiO_2. For instance, Zhao et al. reported the enhanced photocatalytic H_2 generation efficiency of Bi-doped TiO_2 from glycerol solution [19]. Fujita et al. studied the photocatalytic H_2 generation from aqueous formic acid solutions using an NiO/TiO_2 composite [6]. Chang et al. also reported the improved photocatalytic H_2 production from glycerol solutions using ZnO-ZnS/graphene photocatalysts at room temperature [3]. Montini et al. also studied the photocatalytic H_2 production from aqueous solution of ethanol and glycerol using a nanostructured Cu/TiO_2 photocatalyst [20]. Liu et al. also reported the superior photocatalytic hydrogen production efficiency of synthesized ZnO/ZnS–PdS nanorods from aqueous glycerol solution [15]. Vaiano et al. showed the excellent photocatalytic hydrogen production ability of Cu-doped ZnO from glycerol aqueous solution [21]. Manzoor et al. exposed the enhanced photocatalytic H_2 production performance for Cu-incorporated ZnO nanocomposites from methanol solution [1].

In addition, simultaneous metal deposition on the ZnO and TiO_2 nanoparticles for photocatalytic H_2 generation have been investigated. For example, Suhag et al. reported photocatalytic H_2 generation from a formic acid solution using TiO_2 powder and TiO_2 nanotubes with the aid of simultaneous Rh deposition [22,23]. Gomathisankar et al. improved the photocatalytic hydrogen generation using TiO_2 with the aid of simultaneous Au and Pd deposition from an aqueous solution [24]. Gomathisankar et al. also studied photocatalytic hydrogen generation using ZnO with simultaneous photo deposition of Cu from a methanol solution [25].

In the literature, it was reported that Cu catalyst was able to enhance the photocatalytic H_2 production efficiency of ZnO and TiO_2 [21,26]. Moreover, ZnO has a slightly lower band gap and higher photocatalytic activity compared to TiO_2 photocatalyst [2]. Recently, Vaiano et al. reported the photocatalytic hydrogen production from glycerol aqueous solution using Cu-doped ZnO [21]. In the study, the Cu-doped ZnO was synthesized by a precipitation method before the hydrogen production. Therefore, scant information regarding photocatalytic H_2 generation using ZnO from aqueous glycerol solution with simultaneous photo-deposition of Cu is available.

The present work deals mainly with photocatalytic biohydrogen production from biomass-derivative glycerol solution with the simultaneous photo-deposition of Cu. Moreover, the study focuses on the effects of the concentration of glycerol solution, Cu ion concentration, and reaction temperature on the generation of hydrogen. The possible mechanism for photocatalytic hydrogen production using ZnO from aqueous glycerol solution with simultaneous photo-deposition of Cu is proposed. The developed hydrogen production method is cost effective and environmentally friendly.

2. Materials and Methods

2.1. Chemicals and Materials

The photocatalyst ZnO was obtained from Sigma-Aldrich, Tokyo, Japan (BET specific surface area 15–25 m^2/g, mean particle size 50–70 nm). A standard stock solution of Cu^{2+} (1000 mg L^{-1}) was prepared by the dissolution of $CuCl_2$ (Sigma-Aldrich, Tokyo, Japan) in ultrapure water. Glycerol (84–87% purity; Kanto Chemical Co., Inc., Tokyo, Japan) was used without additional purification. Laboratory-pure water was found from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan), resulting in a resistivity of >18 MΩ cm.

2.2. Photocatalytic Hydrogen Production

The hydrogen generation experiments with ZnO nanopowder were carried out by using simultaneous Cu metal deposition. A pyrex vessel reactor of 150 mL (inner volume, 123 mL) was used for the photocatalytic hydrogen generation from aqueous glycerol solution. Typically, 50 mg of the ZnO nanopowder was added to 40 mL of the aqueous glycerol solution. Then, a Cu ion solution with a Cu ion concentration of 100 mg L^{-1} was added to the reactor. A 15 W black lamp with an emission of about 352 nm (Toshiba Lighting & Technology Corp., Tokyo, Japan) was positioned to the one side of the pyrex vessel reactor as a light source. The light intensity was measured by a UV radio meter (UIT-201, Ushio Inc., Tokyo, Japan) and the value was 0.25 mW cm^{-2}. The ZnO nanopowder was constantly stirred in the aqueous glycerol solution by a magnetic stirrer during irradiation by light. Using a hot stirrer, the reactor temperature was kept constant at 50 °C. The reactor was closed with a silicon septum. The irradiation time was 3 h. The produced gas was extracted from the upper portion of the reactor with a micro syringe (ITO, Co., Ltd., Tokyo, Japan) and analyzed by gas chromatography (GL Sciences, GC-3200, Tokyo, Japan) with a thermal conductivity detector. A stainless column (4 m long, 2.17 mm i.d.) packed with a Molecular Sieve 5A (mesh, 60–80) was used for the separation. The carrier gas was 99.99% argon gas (Kawase Sangyo Co., Ltd., Kuwana, Mie, Japan). The temperature settings of the GC were 50 °C for the injection, column, and detector. The flow rate of the carrier gas was 7.0 mL min^{-1}. The analysis time and injected sample volume for analysis were 15 min and 250 μL, respectively. In order to inspect the reproducibility of H_2 production, all experiments were carried out in triplicate and relative standard deviations (RSDs) were observed within 10%. Since the reproducibility for the photocatalytic H_2 production was very good, the error bars for H_2 production were only added in Figure 1 to represent typical cases.

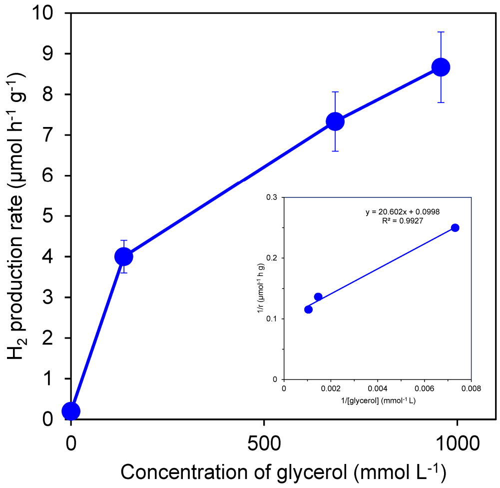

Figure 1. Effect of glycerol concentration on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; Cu concentration, 30 mg L^{-1}; reaction time, 3 h; reaction temperature, 50 °C. Inset figure: Fitting plot of 1/r versus 1/C.

An analysis for copper determination was carried out with a SHIMADZU AA-7000 equipped with an electrothermal graphite atomizer (GFA-7000A), an auto-sampler (ASC-7000), and a deuterium lamp background corrector (Kyoto, Japan).

3. Results and Discussion

3.1. Effect of Glycerol Concentration

In the photocatalytic H_2 production reaction, glycerol can act as hole scavenger [27]. It can be used to reduce the backward reaction of water formation from hydrogen and oxygen on the photocatalyst surface. The effect of glycerol concentration on photocatalytic hydrogen production using ZnO (50 mg) with the aid of instantaneous Cu photo-deposition (30 mg L^{-1}) was inspected at 50 °C temperature. The results are shown in Figure 1.

It was observed that a very small amount of hydrogen was generated from the pure water. However, the photocatalytic hydrogen production was enhanced by the increasing concentration of glycerol solution. Finally, the amount of hydrogen production remained nearly constant in the instance in which above 7.0% v/v (958 mmol L^{-1}) of aqueous glycerol solution was used. The active sites of the ZnO surface were saturated with increasing glycerol concentration, which might result in photocatalytic hydrogen generation with constant efficiencies. Similar results were reported for photocatalytic hydrogen generation from glycerol solution using an NiO/TiO_2 catalyst [6].

The observed change of the H_2 generation with the glycerol concentration may indicate that the adsorption of glycerol on the catalyst obeys the mechanism of the Langmuire–Hinshelwood model. The kinetic equation can be stated as Equation (1).

$$Rate = \frac{kK[glycerol]}{1 + K[glycerol]} \tag{1}$$

where K is the adsorption coefficient of the glycerol molecule on the irradiated surface of the Cu-deposited ZnO catalyst and k is the surface pseudo-first order rate constant. At high concentrations of glycerol ($K[glycerol] >> 1$), the rate of H_2 generation should persist constantly and follow zero-order kinetics (rate $\approx k$). In contrast, at low concentrations ($K[glycerol] << 1$), the rate of H_2 generation should be proportional to the concentration of glycerol and follow first order kinetics with respect to the concentration of glycerol (rate $\approx kK[glycerol]$) with an apparent rate constant kK. The kinetic parameters k and K were deduced from the graph using data fit to the curve governed by the kinetic equation of the Langmuire–Hinshelwood model.

$$1/r = \frac{1 + K[glycerol]}{kK[glycerol]} \tag{2}$$

$$1/r = \frac{1}{kK[glycerol]} + \frac{1}{k} \tag{3}$$

The reciprocal of the hydrogen production rate was plotted against the reciprocal of glycerol concentration, as shown in the inset figure in Figure 1. The deduced adsorption coefficient, K, and pseudo-first order rate constant, k, were 0.00484 $mmol^{-1}$ and 10 µmol h^{-1} g^{-1}, respectively. Figure 2 shows a graphical presentation of the data fit using the deduced kinetic parameters k and K. The experimental results are plotted against the predicted results based on the Langmuire–Hinshelwood kinetic law [24].

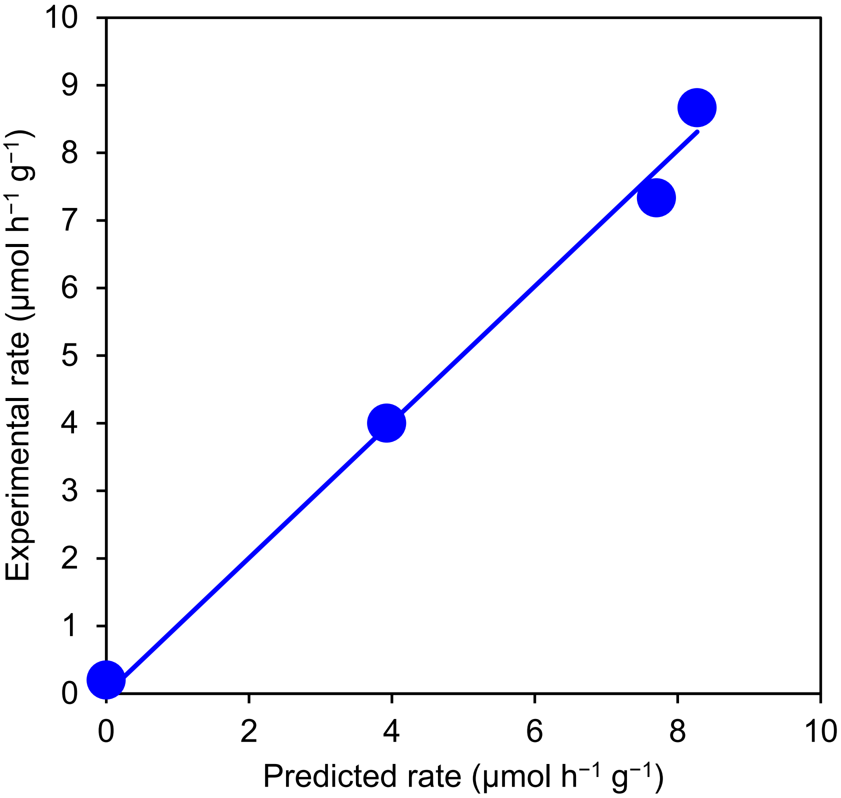

Figure 2. Graphical display of Langmuire–Hinshelwood kinetic data fit.

3.2. Effect of Cu Ion Concentration

The effect of Cu^{2+} ion concentration on the photocatalytic hydrogen production from glycerol solution (958 mmol L^{-1}) using ZnO (50 mg) with simultaneous deposition was examined at 50 °C temperature. As shown in Figure 3, it was observed that with increasing Cu^{2+} ion concentration until 100 mg L^{-1}, the amount of H_2 production was sharply increased. If we assume that all the Cu^{2+} ions from the 100 mg L^{-1} solution were deposited on the ZnO surface after the reaction, the Cu content on the ZnO photocatalyst would be 8 wt%. Since a very small amount of hydrogen was produced in the absence of Cu^{2+} ions, the amount of hydrogen production was enhanced by about 34 times in addition to the 8 wt% of Cu on the ZnO surface with the aid of simultaneous deposition. The improved electron hole pair separation power of ZnO by the photo deposition of Cu metal may be responsible for the enhanced photocatalytic H_2 production. However, there was little dramatic change in the increase in hydrogen production after the addition of a Cu^{2+} ion concentration of 100 mg L^{-1}. The light filtration by the deposited Cu, the partial blockage of the surface-active site for ZnO in the oxidative branch during the photoreaction, the deterioration of catalytic activity of Cu/ZnO nanoparticles at the enlargement of Cu ions, and the establishment of recombination centers by excessive Cu metal clusters could be responsible for the constant amount of hydrogen production at higher concentrations of Cu [25,28]. After the photocatalytic H_2 production reaction, ZnO powders were filtered using 0.45 μm of Advantec membrane filter. The concentration of Cu in the filtrate of ZnO powders was estimated by atomic absorption spectroscopy. It was noticed that Cu could not be detected in the solution. The results indicated that all of the Cu in the aqueous glycerol solution was deposited onto the surface of ZnO during the photocatalytic H_2 production reaction.

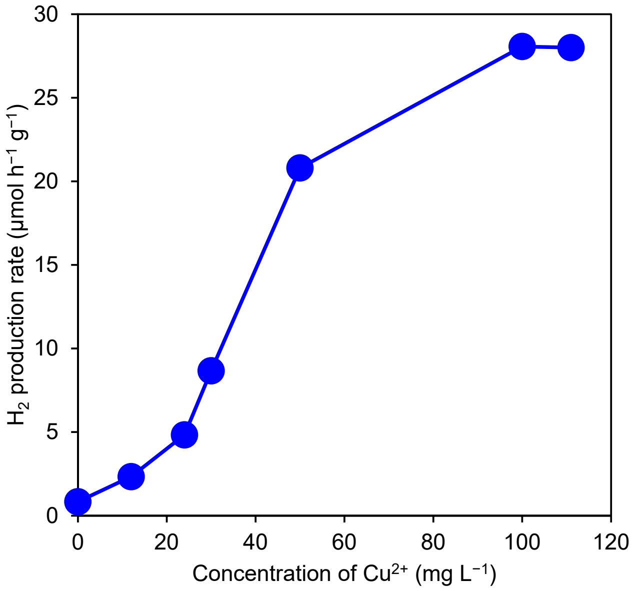

Figure 3. Effect of Cu^{2+} concentration on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; glycerol, 7% *v*/*v* (958 mmol L^{-1}); reaction time, 3 h; reaction temperature, 50 °C.

3.3. Effect of Temperature

The effect of temperature on photocatalytic hydrogen production using ZnO (50 mg) with the aid of simultaneous Cu photo-deposition (100 mg L^{-1}) from aqueous solution of glycerol (958 mmol L^{-1}) was investigated. The results are revealed in Figure 4. It was observed that the rate of hydrogen production improved with the increase in the reaction temperature. The results showed that the interfacial charge transfer may be influenced by the reaction temperature. Thus, the photocatalytic hydrogen production was dependent on the temperature of the reaction [29]. A similar result was previously reported for photocatalytic hydrogen production from formic acid using TiO_2 with the aid of simultaneous Rh photo-deposition [22].

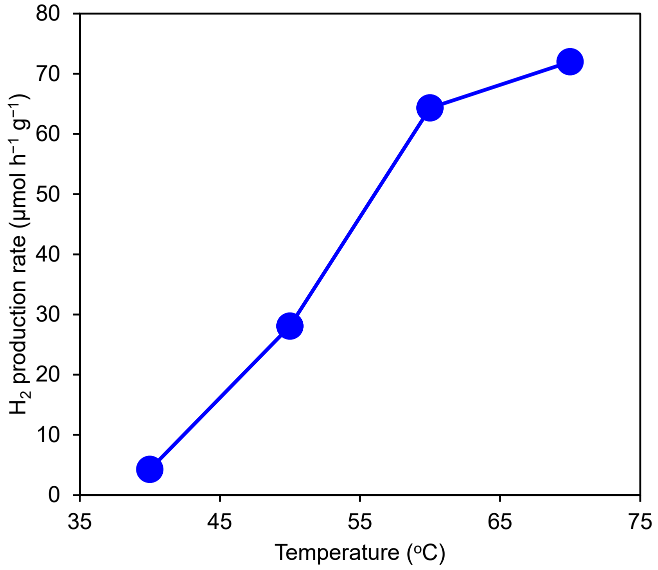

Figure 4. Effect of temperature on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; glycerol, 7% *v*/*v* (958 mmol L^{-1}); Cu^{2+} concentration, 100 mg L^{-1}; reaction time, 3 h.

3.4. Reaction Mechanism

Based on the previously reported literature [24,25], a possible mechanism for the photocatalytic H_2 generation from aqueous glycerol solution using ZnO with the aid of simultaneous photo deposition of Cu metal has been proposed as follows. As shown in Figure 5a, holes and electrons can be generated under the irradiation of light on the surface of ZnO. The photogenerated electrons are excited to the conductance band, while holes are created in the valence band (Equation (4)). Then, copper ions are reduced to Cu metals on the ZnO surface by reacting with photogenerated electrons in the conductance band for the establishment of metallic clusters (Equations (5) and (6)). Next, other photo-generated electrons transfer to the surface of the Cu nanoparticles and improve the photogenerated charge separation. The transfer of electrons to Cu nanoparticles is continuous until the fermi level approaches the conduction band edge of ZnO (Equations (7) and (8)). Furthermore, as shown in Figure 5b, the photogenerated electrons and holes participate in a redox reaction at the interface between the ZnO and the glycerol solution. The holes reacted with water to form hydroxyl radicals (•OH) and proton ions (H^+) (Equation (9)). Based on literature reports [30–32], it was proposed that glycerol molecules were adsorbed on the surface of ZnO and reacted with the formed hydroxyl radicals to degrade into CO_2 and H^+ as shown in Figure 6. Since hydrogen atoms can generally be extracted by the hydroxyl radicals from hydroxylated carbon more effectively, relative to from non-hydroxylated carbon, the hydroxyl radicals are primarily reacted with alcohols to produce aldehyde, which is then further oxidized to produce carboxylic acid. Hence, after the adsorption of glycerol onto ZnO, glycerol reacts with hydroxyl radicals to oxidize to glyceraldehyde through 1,1,2,3-tetrahydroxy propane. The generated glyceraldehyde is further oxidized to produce glyceric acid. The subsequent oxidation of glyceric acid by the •OH radical produces glycolic acid due to the C–C bond cleavage. Additionally, the deprotonation from carboxylic acid by the hydroxyl radical results in the formation of the carboxyl radical (RCO_2^-), inducing the decarboxylation process of carboxylic acids.

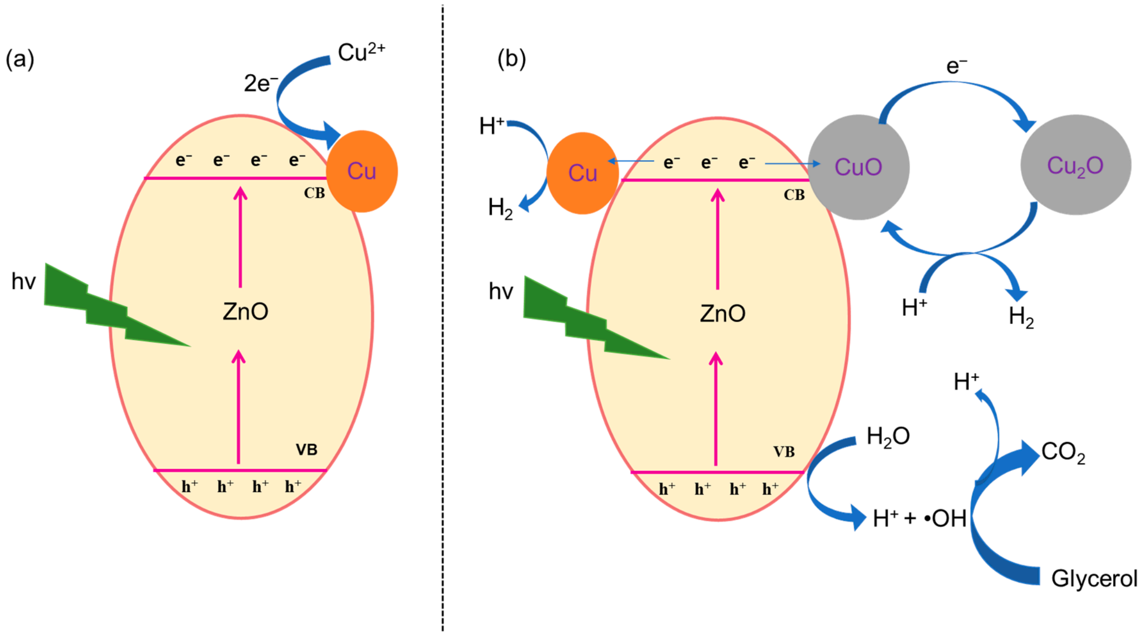

Figure 5. Schematic diagram for mechanism of photocatalytic hydrogen production from formic acid solution using the ZnO photocatalyst with the simultaneous photo-deposition of Cu. (**a**) the process of the generation of holes and electron pairs under the irradiation of light on the surface of ZnO, followed by the photodeposition of Cu. (**b**) the redox reaction at the interface between the ZnO and the glycerol solution.

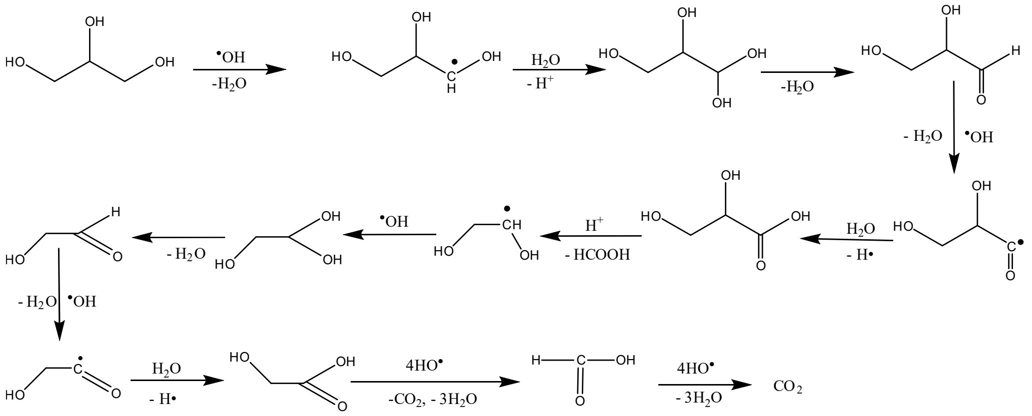

Figure 6. Proposed reaction mechanism for oxidation of glycerol.

Glycolic acid undergoes further oxidation to form formic acid and ultimately carbon dioxide. The H^+ ions are also formed in the several steps of the reaction. After that, produced proton ions are reduced to H_2 by accepting the electrons on the surface of Cu metals (Equation (10)).

$$\text{nanosized ZnO} + h\nu \rightarrow \text{electron(CB)} + \text{hole(VB)} \tag{4}$$

$$Cu^{2+} + 2e^-(\text{nanosized ZnO}) \rightarrow Cu/ZnO \tag{5}$$

$$ZnO\text{-}n(Cu) \rightarrow ZnO\text{-}Cu_n \tag{6}$$

$$ZnO\text{-}Cu_n + h\nu \rightarrow ZnO(e^-{}_{CB} + h^+{}_{VB})\text{-}Cu_n \tag{7}$$

$$ZnO(e^-{}_{CB} + h^+{}_{VB})\text{-}Cu_n \rightarrow ZnO(h^+{}_{VB})\text{-}(Cu_n)(\text{electron}) \tag{8}$$

$$H_2O + h^+(\text{nanosized ZnO}) \rightarrow H^+ + \bullet OH \tag{9}$$

$$2H^+ + 2e^-(Cu_n) \rightarrow H_2 \tag{10}$$

In addition, it was observed that during the H_2 generation process, the white-colored suspension of ZnO turned gradually black. The black color was observed due to the formation of CuO on the ZnO surface [33]. It was assumed that CuO and Cu_2O may be formed as a result of the reaction of a portion of deposited Cu metal with the dissolved oxygen in the solution. Since CuO is more stable than Cu_2O, the Cu_2O can be readily oxidized to CuO, and the proton can be reduced to produce H_2 gas.

Yang et al. [34] reported the improving glycerol photoreforming hydrogen production over Ag_2O-TiO_2 catalysts by enhanced colloidal dispersion stability. In the work, a novel method of mixing Ag_2O-TiO_2 photocatalysts with different morphologies was implemented to promote colloidal dispersion stability, thereby improving hydrogen production performance. A series of Ag_2O-TiO_2 nanoparticles with different morphologies were synthesized and their dispersion stabilities in aqueous phase were investigated individually. Two types of Ag_2O-TiO_2 particles with different morphologies under certain proportions were mixed and suspended in glycerol aqueous solution without adding any dispersant for enhancing dispersion stability while reacting. A 300W Xe arc lamp (50 W, 320–780 nm) was used as a light source and vertically placed 10 cm away from the top of the photocatalytic reactor. The focused light intensity and area on the flask for xenon lamp were ca. 120 mW/cm^2 and 0.2 cm^2, respectively. The H_2

evolution rate, adsorption coefficient, K, and pseudo-first order rate constant, k, were about 104 μmol h^{-1} g^{-1}, 0.00462 L $mmol^{-1}$, and 10.1 μmol h^{-1} g^{-1}, respectively.

Wang et al. [35] investigated the improved hydrogen production by glycerol photoreforming over Ag_2O-TiO_2 nanocomposite-mixed oxide synthesized by a sol-gel method. In the study, the hydrogen production from photocatalytic reforming of glycerol aqueous solution was optimized over Ag_2O-TiO_2 nanocomposite-mixed oxide catalysts with catalysts of variable compositions (0.75–6.75 wt% Ag_2O) synthesized by a sol-gel method. A parallel light source system (50 W, 320–780 nm) was used as a light source to trigger the photocatalytic reaction. The results of photocatalytic performance showed that H_2-production activity and the reaction rate of TiO_2 were significantly enhanced by mixing Ag_2O. Under the optimal conditions, the H_2 generation rate was approximately 234 μmol h^{-1} g^{-1}.

Choi et al. [1] studied the optical properties of Cu-incorporated ZnO (Cu_xZn_yO) nanoparticles and their photocatalytic hydrogen production performances. In the work, the Cu (0.1, 0.5, 1.0, and 5.0 mol%)-incorporated ZnO nanoparticles (Cu_xZn_yO) were prepared by a conventional hydrothermal method. The H_2 production activity of Cu-inserted ZnO catalysts was higher than the pure ZnO catalyst. Among the different photocatalysts, the $Cu_{0.01}Zn_{0.99}O$ catalyst having a 1.0 mol% of Cu showed the higher H_2 production activity. The highest photocatalytic water-methanol splitting reaction rate was 5.84 μmol h^{-1} g^{-1}.

Monzoor et al. [2] studied the enhanced photocatalytic activity of hydrogen evolution through Cu-incorporated ZnO nanocomposites. In the research, the efficient nanocomposites of ZnO doped with varying percentage of copper (0.0, 0.01, 0.03, and 0.05 mol.%) were synthesized by sol-gel method to analyze the H_2 evolution. UV radiations emitted at 365 nm were used. Cu-incorporated ZnO catalysts caused an enhancement in H_2 production from 1.2 μmol h^{-1} g^{-1} to 6.9 μmol h^{-1} g^{-1}.

Gomathisankar et al. [25] investigated the enhanced photocatalytic hydrogen production from aqueous methanol solution using ZnO with simultaneous photodeposition of Cu. In the work, the simultaneous deposition for such metals as Ag, Au, Cu, Ni, Pd, Pt, and Rh were evaluated for the H_2 production from an aqueous methanol solution. As a result, the addition of Cu ions effectively improved photocatalytic hydrogen evolution. The photocatalytic hydrogen production using a ZnO photocatalyst with the aid of simultaneous deposition of Cu was approximately 130 times better than those obtained with bare ZnO. The H_2 evolution rates under the irradiation of UV and visible light were 59.3 and 0.4 μmol h^{-1} g^{-1}, respectively.

In the present research work, the photocatalytic bio-hydrogen production efficiency from aqueous glycerol solution using ZnO nanopowder with the aid of simultaneous photo deposition of Cu metal was better, compared with those obtained with only ZnO. The action of Cu as a co-catalyst and the enhancement of photogenerated charge separation would be responsible for the improvement of the photocatalytic H_2 production reaction.

Table 1 shows the comparison of this work with reported photocatalytic bio-hydrogen (green H_2) productions. The results for the present work were almost same or superior relative to the reported photocatalytic green H_2 production.

Table 1. Comparison of photocatalytic bio-hydrogen productions.

Photocatalyst	Medium	Light Source	H_2 Generation (μmol h^{-1} g^{-1})	Ref.
Ag_2O-TiO_2	Glycerol	300W Xe	104	[34]
Ag_2O-TiO_2	Glycerol	50W Xe	234	[35]
Cu/ZnO	Methanol	UV	6.9	[1]
Cu/ZnO	Methanol	365 nm	5.84	[2]
Cu/ZnO	Methanol	UV	59.3	[25]
Cu/ZnO	Methanol	>400 nm	0.4	[25]
in situ Cu-deposited ZnO	Glycerol	Black light	72	This work

4. Conclusions

In short, it was found that the simultaneous photo-deposition of Cu on ZnO increased the photocatalytic hydrogen production from aqueous glycerol solution. The impact of glycerol concentration on hydrogen generation was fitted with the Langmuire–Hinshelwood model. The photocatalytic hydrogen generation rate with the aid of the simultaneous photodeposition of 8 wt% Cu metal on ZnO was about 34 times better than that obtained with the bare ZnO, from 7% v/v (958 mmol L^{-1}) of aqueous glycerol solution at 50 °C temperature. During the photocatalytic hydrogen generation process, all of the Cu in the aqueous solution of glycerol became embedded onto the surface of ZnO. The deposition of copper (copper oxide) on the surface of ZnO may be an effective method to produce a good catalytic active site and fast separation of electron–hole pairs.

Author Contributions: Conceptualization, M.H.S.; investigation, M.F.; data curation, M.F.; writing—original draft preparation, M.H.S. and I.T.; writing—review and editing, H.K. and A.K.; supervision, S.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by Grant-in-Aid for Scientific Research (B) 21H03642 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge S. Nishimoto for the experimental supports.

Conflicts of Interest: All experiments were conducted at Mie University. Any opinions, findings, conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

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