Communication

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

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

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Abstract: The 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 concentration of glycerol solution, Cu ion concentration and reaction temperature on biohydrogen generation were investigated. The photocatalytic biohydrogen production rate increased with increasing the concentration of aqueous glycerol solution, 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 with the increasing temperature. The possible mechanisms for oxidation of glycerol solution and photocatalytic hydrogen generation were proposed.

Keywords: hydrogen production; aqueous glycerol solution; simultaneous Cu deposition; ZnO; photocatalyst

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 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].

The photocatalytic H_2 production from glycerol can be environmentally responsive and cost effective. Hence, photocatalytic H_2 production from glycerol has been a more attractive choice, owing to its less 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 like 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]. Lower photoactivities of ZnO and TiO_2 are the main limitations for the 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 the lower photo activity of ZnO and TiO_2 in the hydrogen production reaction [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 improve the photocatalytic H_2 generation performance of the ZnO and TiO_2. For instance, Zhao et al. reported the enhanced the 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 NiO/TiO_2 composite [6]. Chang et al. reported the improved photocatalytic H_2 production from glycerol solutions using ZnO-ZnS/graphene photocatalysts at room temperature [3]. Montini et al. studied the photocatalytic H_2 production from aqueous solution of ethanol and glycerol using nanostructured Cu/TiO_2 photocatalyst [20]. Liu et al. reported the better photocatalytic hydrogen production efficiency of synthesized ZnO/ZnS–PdS nanorods from aqueous glycerol solution [15]. Vaiano et al. have shown 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, the simultaneously metal deposition on the ZnO and TiO_2 nanoparticles for the photocatalytic H_2 generation have been also investigated. For example, Suhag et al. reported the photocatalytic H_2 generation from formic acid solution using TiO_2 powder and TiO_2 nanotube with the aid of simultaneous Rh deposition [22,23]. Gomathisankar et al. have shown improved the photocatalytic hydrogen generation using TiO_2 with the aid of simultaneous Au and Pd deposition from aqueous solution [24]. Gomathisankar et al. also studied the photocatalytic hydrogen generation using ZnO with simultaneous photo deposition of Cu from 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 slightly lower band gap and higher photocatalytic activity, compared to TiO_2 photocatalyst [2]. Although Cu/ZnO composite has previously been applied to photocatalytic hydrogen generation from aqueous glycerol solution, there is little information on the photocatalytic H_2 generation on ZnO from aqueous glycerol solution with simultaneous photo-deposition of Cu. The present work has dealt mainly with the photocatalytic biohydrogen production from biomass derivative glycerol solution with the simultaneous photo-deposition of Cu.

2. Materials and Methods

2.1. Chemicals and materials

The photocatalyst ZnO was obtained from Sigma-Aldrich, 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) in pure water. Glycerol (84%–87%; Kanto Chemical Co., Inc., 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 MU cm.

2.2. Photocatalytic Hydrogen Production

The hydrogen generation experiments with ZnO nanopowder were carried out by using simultaneous Cu metal deposition. The pyrex vessel reactor (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, the solution of Cu ion was added to the reactor, and the concentration of Cu ion was 100 mg L^{-1}. 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 the irradiation of 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, Japan) with a thermal conductivity detector. The 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., 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 analysis sample amount were 15 mins and 250 μL, respectively. The reproducibility of H_2 production was inspected, and relative standard deviations (RSDs) were observed within 10% for more than three runs.

3. Results and Discussion

3.1. Effect of Glycerol Concentration

In the photocatalytic H_2 production reaction, glycerol could act as hole scavenger. 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 with the aid of instantaneous Cu photo-deposition was inspected. The results are shown in Figure 1.

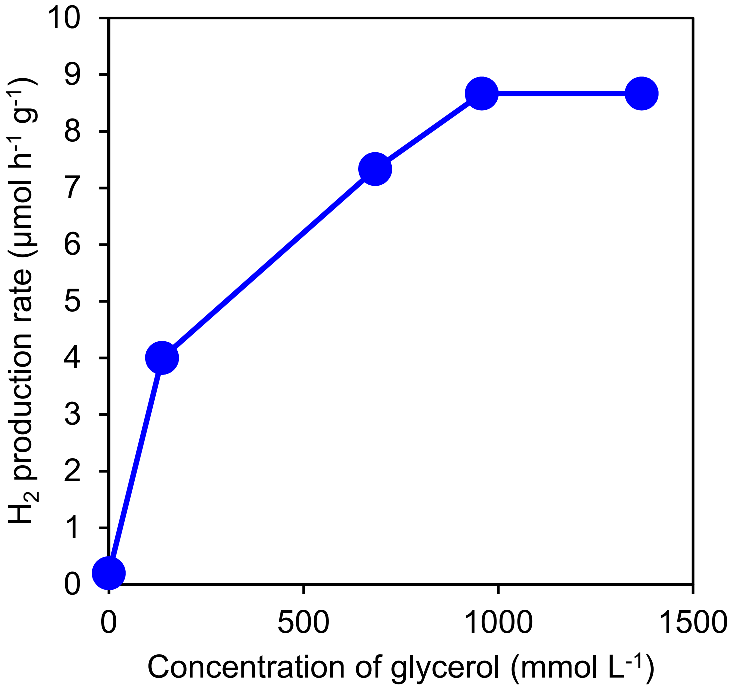

Figure 1. Effect of glycerol concentration on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; Cu concentration, 30 mg L^{-1}; reaction time, 3 h; reaction temperature, 50 °C.

It was observed that very small amount of hydrogen was generated from the only 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 of using above 7.0% vol/vol (958 mmol L^{-1}) of aqueous glycerol solution. The active sites of ZnO surface were saturated with increasing glycerol concentration, which might result in the photocatalytic hydrogen generation with the constant efficiencies. Similar results were reported for photocatalytic hydrogen generation from glycerol solution using NiO/TiO_2 catalyst [6].

The observed change of the H_2 generation with the glycerol concentration may indicate it 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).

$$Rate = \frac{kK[glycerol]}{1+K[glycerol]} \quad (1)$$

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 constant and follow the zero-order kinetics (rate ≈ 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 the first order kinetics with respect to the concentration of glycerol (rate ≈ $kK[glycerol]$) 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. The deduced adsorption coefficient, K, and pseudo-first order rate constant, k, were 0.00462 L mmol^{-1} and 10.1 µmol h^{-1} g^{-1}, respectively. Figure 2 is the graphical presentation of the data fit using the deduced kinetic parameters k and K. The experimental results are plotted against the predicted ones based on the Langmuire-Hinshelwood kinetic law [24].

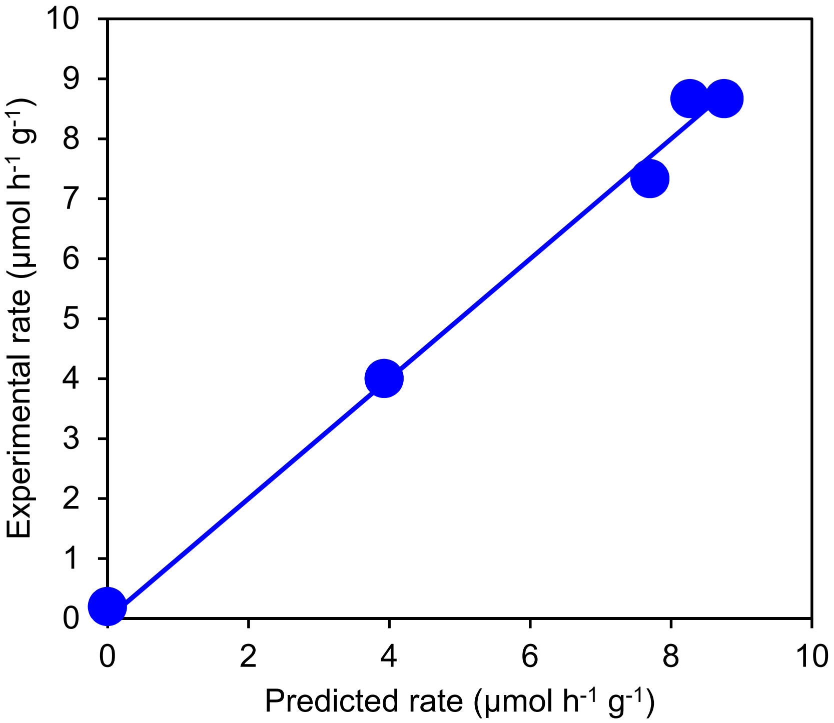

Figure 2. Graphical display of Langmuire-Hinshelwood kinetic data fit.

3.2. Effect of Cu Ion Concentration

The effect of Cu^{2+} ion concentration on the photocatalytic hydrogen production using ZnO with simultaneous deposition was examined. 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 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 the 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 enhanced photocatalytic H_2 production. However, there was little dramatic change in the increase in hydrogen production after the addition of 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 ion, and the establishment of recombination centers by excessive Cu metal clusters could be responsible for the constant amount

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of hydrogen production at higher concentrations of Cu [25,27]. After the photocatalytic H_2 production reaction, ZnO powders were filtered using 0.45 mm of Advantec membrane filter. The concentration of Cu in the filtrate of ZnO powders was estimated by flame atomic absorption spectroscopy. It was noticed that Cu could not be detected in the solution. The results indicated that all the Cu in the aqueous glycerol solution was deposited onto the surface of ZnO during the photocatalytic H_2 production reaction.

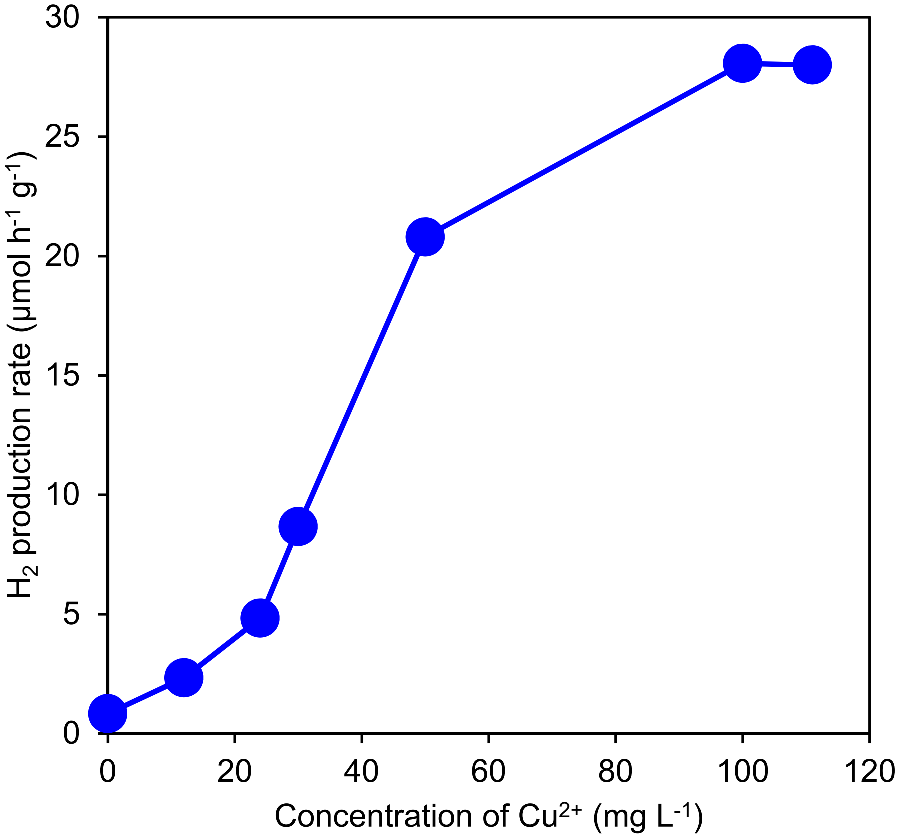

Figure 3. Effect of Cu^{2+} concentration on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; glycerol, 7% vol/vol (958 mmol L^{-1}); reaction time, 3 h; reaction temperature, 50 °C.

3.3. Effect of Temperature

The effect of temperature on photocatalytic hydrogen production using ZnO with the aid of simultaneous Cu photo-deposition from aqueous solution of glycerol 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 gave it 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 [28]. Similar result was previously reported for photocatalytic hydrogen production from formic acid using TiO_2 with the aid of simultaneous Rh photo-deposition [22].

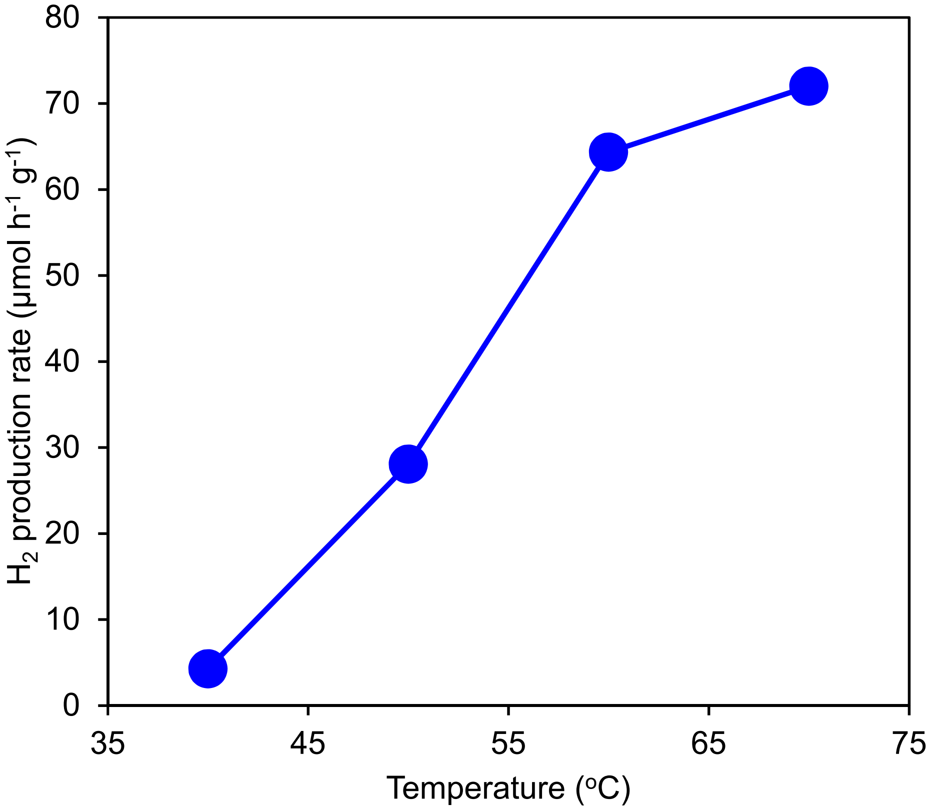

Figure 4. Effect of temperature on photocatalytic H_2 production using ZnO from glycerol solution with simultaneous photo-deposition of Cu. ZnO, 50 mg; glycerol, 7 % vol/vol (958 mmol L^{-1}); Cu^{2+} concentration, 100 mg L^{-1}; reaction time, 3 h.

3.4. Reaction Mechanism

Based on the previous reported literatures [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 5 (a), 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 (Equ. 2). 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 (Equs. 3 and 4). Next, another 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 (Equs. 5 and 6). Furthermore, as shown in Figure 5 (b), the photogenerated electrons and holes participate in a redox reaction at the interface between ZnO and glycerol solution. The holes reacted with water to form hydroxyl radical (•OH) and proton ion (H^+) (Equ. 7). Based on literature reports [29–31], 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. In brief, after the adsorption of glycerol onto ZnO, glycerol has been reacted with hydroxyl radicals for oxidizing 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. 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 (Equ. 8).

$$\text{nanosized ZnO} + h\nu \longrightarrow \text{electron(CB)} + \text{hole(VB)} \qquad (2)$$

$$Cu^{2+} + 2e^{-}(\text{nanosized ZnO}) \longrightarrow Cu/ZnO \quad (3)$$

$$ZnO\text{-}n(Cu) \longrightarrow ZnO\text{-}Cu_n \quad (4)$$

$$ZnO\text{-}Cu_n + h\nu \longrightarrow ZnO(e^{-}_{CB} + h^{+}_{VB})\text{-}Cu_n \quad (5)$$

$$ZnO(e^{-}_{CB} + h^{+}_{VB})\text{-}Cu_n \longrightarrow ZnO(h^{+}_{VB})\text{-}(Cu_n)(\text{electron}) \quad (6)$$

$$H_2O + h^{+}(\text{nanosized ZnO}) \longrightarrow H^{+} + \bullet OH \quad (7)$$

$$2H^{+} + 2e^{-}(Cu_n) \longrightarrow H_2 \quad (8)$$

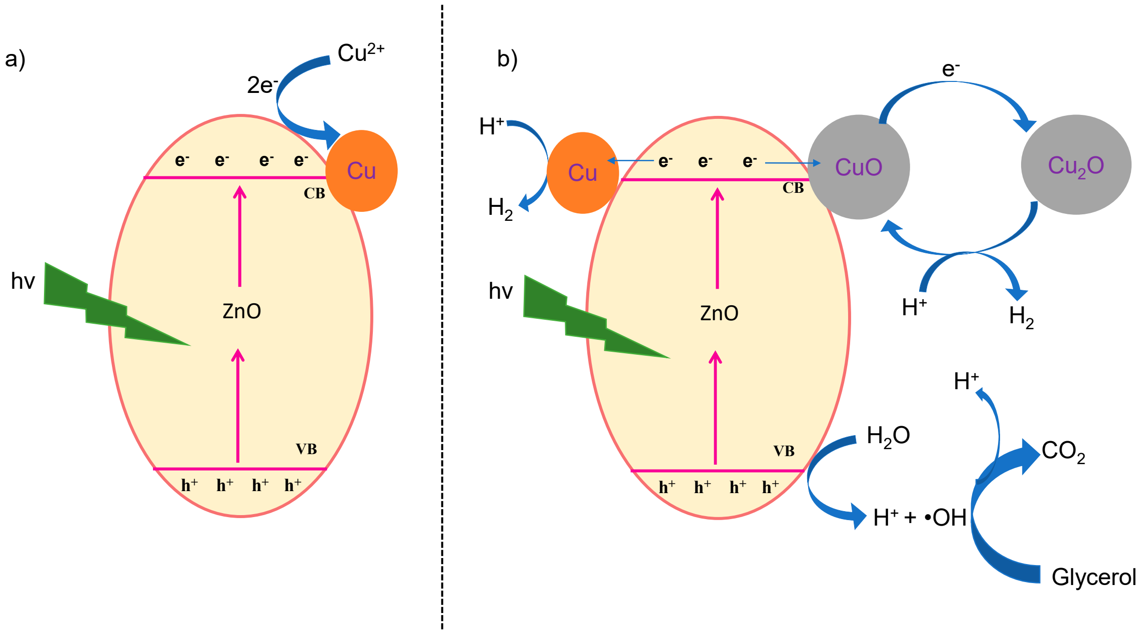

Figure 5. Schematic diagram for mechanism of photocatalytic hydrogen production from formic acid solution using the ZnO photocatalyst with the simultaneous photo-deposition of Cu.

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 [32]. 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.

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 cocatalyst and the enhancement of photogenerated charge separation would be responsible for the improvement of the photocatalytic H_2 production reaction.

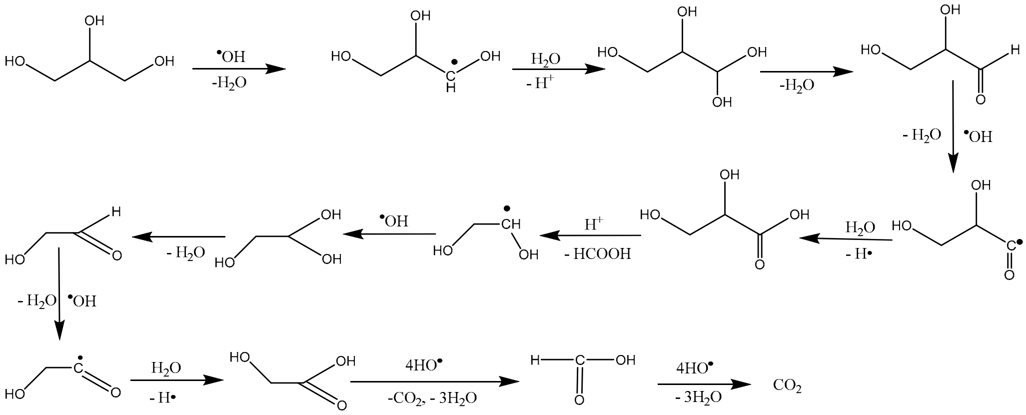

Figure 6. Proposed reaction mechanism for oxidation of glycerol.

4. Conclusions

In short, it was inspected that the simultaneous photo-deposition of Cu on ZnO increased the photocatalytic hydrogen production from aqueous glycerol solution. The photocatalytic hydrogen generation rate with the aid of the simultaneous photo deposition of 8 wt% Cu metal on ZnO was about 34 times better than that obtained with the bare ZnO, from 7% vol/vol (958 mmol L^{-1}) of aqueous glycerol solution at 50 °C temperature.

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