Front. Chem. China 2009, 4(1): 32–38
DOI 10.1007/s11458-009-0019-6

RESEARCH ARTICLE

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Photocatalytic hydrogen generation using glycerol wastewater over Pt/TiO_2

Abstract Using glycerol as electron donor, photocatalytic hydrogen generation over Pt/TiO_2 was investigated. The results show that glycerol can not only improve the efficiency of photocatalytic hydrogen generation but can also be decomposed effectively. The factors which affect photocatalytic hydrogen generation, such as irradiation time, initial concentration of the glycerol solution, pH-value of the suspensions and the coexisting substances were studied. The final oxidation products of glycerol were H_2O and CO_2. Glyceraldhyde, glycoladehyde, glycolic acid and formaldehyde were identified as the intermediates. A possible reaction mechanism was discussed.

Keywords photocatalysis, hydrogen generation, glycerol, degradation

1 Introduction

Environmental pollutants and the shortage of energy resources have been two difficult problems that all countries hope to solve urgently. Thus, much attention has been paid to researches on new energy resources and effective environmental cleaning technologies. Photocatalytic splitting of water to hydrogen using a semiconductor as photocatalyst has been regarded as one of the most promising approaches. However, the efficiency of photocatalytic hydrogen evolution is in general very low due to the recombination of the photoinduced electron and the hole, and the back reaction of H_2 and O_2. To inhibit the above two disadvantageous processes, an electron donor can be added into the reaction system as a hole scavenger to achieve high efficiency for hydrogen evolution [1–7]. Many organic pollutants in wastewater are good electron donors. Photocatalytic hydrogen generation has been combined with the destruction of pollutants, which demonstrates that hydrogen generation and destruction of pollutants can be carried out simultaneously [8–13].

Glycerol is an important organic industry and medical material, and is used extensively in organic synthesis and in the pharmaceutical industry. Thus, it often occurs in above-industry wastewater. Also, there are large amounts of glycerol wastewater resulting from industrial soap-making and from fatty acid and biodiesel-making processes. These wastewaters can cause eutrophication of the water-body [14] and result in the shortage of oxygen and death of organisms in the water-body. Thus, it is of interest to combine photocatalytic hydrogen generation with destruction of the pollutant by using it as an electron donor to lower the cost of hydrogen evolution and degrade the pollutant simultaneously. In this paper, using glycerol as electron donor, the reactions of photocatalytic hydrogen generation and degradation of glycerol over a Pt/TiO_2 photocatalyst are investigated.

2 Experiments

2.1 Reagents and preparation of photocatalyst

All reagents were of analytic grade. Photocatalyst TiO_2 with deposited Pt was prepared by photodeposition [1–6]: 1.000 g TiO_2 (anatase, Shanghai Caiyu Co Ltd), 13.34 mL 1.93×10^{-3} mol/L H_2PtCl_6, 1 mL ethanol and 85.66 mL distilled water were mixed, and then the resultant 100 mL suspension was irradiated with a 250 W high pressure Hg lamp for 2 h under stirring to deposit Pt on TiO_2. After filtration and washing with distilled water three times, drying at 393 K for 10 h and milling, 0.5 wt% Pt/TiO_2 was obtained.

2.2 Photocatalytic reaction

A 250 W high pressure Hg lamp was used as the light source, and the photocatalytic reaction was carried out in a Pyrex flask of ca. 190 mL with a flat window at room

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Translated from Journal of Molecular Catalysis, 2008, 22(2) (in Chinese)

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temperature. 100 mL aqueous glycerol solution and 0.040 g 0.5 wt% Pt/TiO_2 were added into the cell. Prior to irradiation, suspensions of the catalyst were carried out in an ultrasonic bath for 5 min and nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen. The reaction mixture (100 mL) inside the cell was maintained in suspension by means of magnetic stirring. The pH of the solution was adjusted by the addition of 0.50 mol/L H_2SO_4 or NaOH. The pH values of the solution were determined on a pHS-3C pH Meter. Chemical oxygen demand (COD) values were measured on a COD-571 Meter using the potassium dichromate method, and the results were calculated in mg/L. The gas product hydrogen was analyzed on a gas chromatograph (zeolite NaX column, N_2 as gas carrier, TCD).

2.3 Adsorption experiment

0.100 g photocatalyst was added into 20 mL 1.00 mmol/L glycerol solutions with pH 3, 7 and 11, respectively, and stirred for 30 min in the dark. The catalyst was removed by centrifugation. COD values of the glycerol solutions were measured before and after adsorption to determine adsorption amount of glycerol on TiO_2.

2.4 Determination of reaction product in liquid phase

After the reaction, the catalyst was removed by centrifugation. The intermediates in reacted solutions were determined by HPLC-MS (High Performance Liquid Chromatography-Mass spectra) and the electrochemical cyclic voltammetry method. Formaldehyde (CH_2O) was detected qualitatively by acetylacetone colorimetry [15].

High Performance Liquid Chromatagraphy conditions were: Hypersil-ODS-C_{18} column (ϕ 4.6 mm × 100 mm, 5 μm), acetonitrile/water ratio of 1.6/98.4(*V*/*V*) as mobile phase solution (whose pH was adjusted to 2.2 with trifluoroacetic acid), flow rate: 0.4 mL/min, and UV detector at 210 nm [16]. Mass spectra conditions were: ionization mode: electrospray ionization (ESI), capillary voltage: 2.8 kV, sampling cone: 30.00 V, extraction cone: 3.00 V, ion source temperature: 120°C, desolving temperature: 350°C at 250 L/h flow rate, mass scan range: m/z 50–120.

The electrochemical experiment was carried out on a three-electrode system at room temperature. The reference electrode, the counter electrode and the working electrode used were a saturated calomel electrode (SCE), a platinum flake and a platinum flake, respectively. The electrodes were cleaned with distilled water in an ultrasonic bath for 10 min. To monitor formed intermediates in the reaction solution, 20 mL 1.00 mol/L NaOH was added into the 20 mL reaction solution, and the cyclic voltammetry curves were obtained under stirring with a magnetic stirrer. The blank experiment was carried out using 0.50 mol/L NaOH to obtain a flat cyclic voltammetry curve.

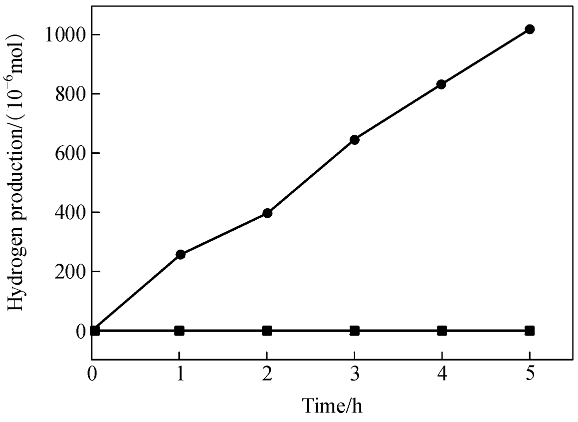

Fig. 1 Amount of photocatalytic H_2 generation as a function of reaction time (solution 100 mL, Co = 0.75 or 0 mmol/L, natural pH)

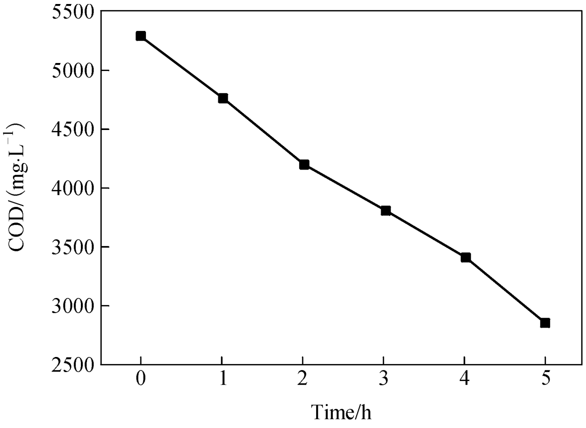

Fig. 2 The COD value of solution as a function of reaction time (solution 100 mL, Co = 0.75 mmol/L, natural pH)

3 Results and discussion

3.1 The reaction time curve

Figure 1 shows that in the absence of glycerol, no hydrogen was detected within 5.0 h of irradiation, whereas in the presence of 0.75 mmol/L glycerol, the amount of H_2 produced increased almost proportionally to the irradiation time within 5.0 h, demonstrating that glycerol markedly increases the efficiency of hydrogen evolution. This result can be attributed to glycerol acting as an electron donor to scavenge photoinduced holes quickly so that the recombination of photoinduced electrons and holes at the semiconductor surface and the back reaction of H_2 and O_2 are inhibited Thus, the hydrogen evolution rate is improved.

Figure 2 describes the change in COD value of the reaction solution under the same reaction conditions as in

Fig. 1. With the increase in reaction time, the COD value decreased almost proportionally to the irradiation time, and the average removal rate of COD was 498.8 mg/(L·h). Because there was no inorganic reductive substance in this system, COD could be used to expresses the relative content of glycerol. After a 5 h irradiation, COD of the glycerol solution decreased by 46.48%, demonstrating that hydrogen evolution and degradation of glycerol can be carried out simultaneously in this reaction system.

3.2 The effect of glycerol concentration

Because the concentration of the electron donor varied continuously in the reaction, in order to determine the initial reaction rate, the reaction time interval should be as short as possible. However, it is important that enough change in the reactant or product be determined during the time interval. Therefore, a 30 min time interval was adopted to determine the initial reaction rate in this investigation.

Figure 3 describes the effect of glycerol concentration on the rate of hydrogen evolution. The rate increased sharply with the increase in the concentration of C_0(glycerol) < 0.75 mmol/L and was almost independent of the initial concentration(C_0) of C_0(glycerol) > 1.50 mmol/L. Thus, the rate varied as a function of C_0 (glycerol) in accordance with a Langmuir-Hinshelwood isotherm, and could be expressed as follows [17]:

$$r_1 = \mathrm{d}C(\mathrm{H}_2)/\mathrm{d}t = k_1 k_2 C_0/(1 + k_2 C_0) \tag{1}$$

where r_1, k_1, k_2 and C_0 represent the initial reaction rate of the hydrogen generation, the reaction rate constant, the adsorption constant of glycerol and the initial concentration of glycerol, respectively. Based on the linear transformation of the curve of Fig. 3, we obtained $k_1 = 4.8 \times 10^{-7}$ mol/min; $k_2 = 1.4 \times 10^2$ L/mol.

When the concentration of glycerol was 1.50 mmol/L, the rate of hydrogen evolution reached its maximum, demonstrating that glycerol, even at low concentrations, can also promote hydrogen evolution effectively.

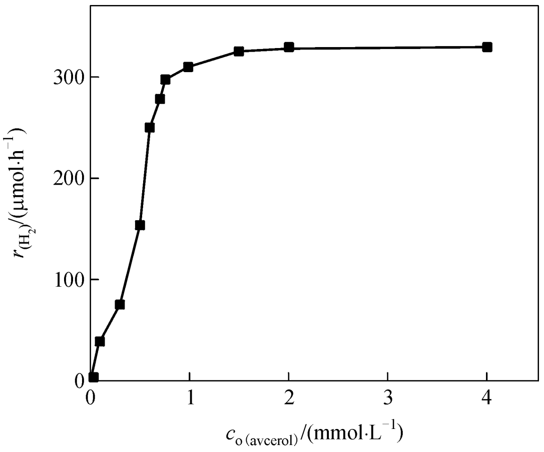

Fig. 3 Initial rate of photocatalytic H_2 generation as a function of C_0 (glycerol) (solution 100 mL, natural pH)

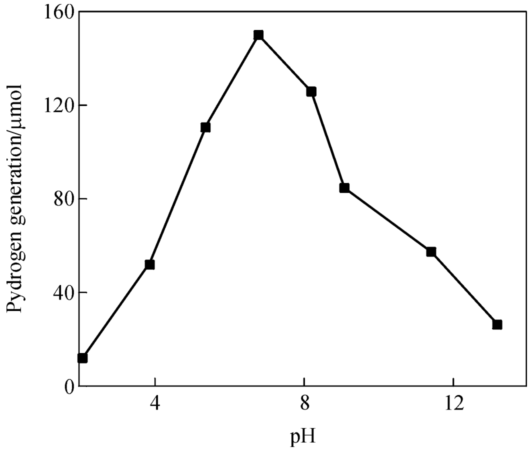

Fig. 4 Amount of photocatalytic H_2 generation as a function of pH-value of the solution (solution 100 mL, Co = 0.75 mmol/L, natural pH)

3.3 Effect of pH

The small amount of deposited Pt changes the pH of the zero point of charge (pHzpc) of TiO_2 [18] a little. Figure 4 shows that at pH = 6.4, using glycerol as electron donor, the hydrogen evolution rate reached a maximum. The pH is close to the pHzpc of TiO_2 (pHzpc of P25 TiO_2 is 6.25). This can relate to the adsorption of glycerol on the photocatalyst. In water solution, there are many surface hydroxyl groups on TiO_2 [19]. Thus, the surface hydroxyl groups on TiO_2 exist mainly in TiOH form at about pHzpc. Glycerol can interact with TiO_2 surface sites via hydrogen bonding to be adsorbed on TiO_2. Because there is a maximal concentration of the surface hydroxyl group at about pHzpc, the amount of photoinduced hydroxyl radicals should be produced largely under irradiation and the adsorption amount of glycerol should also be maximal. To conform this speculation, COD values of glycerol solution before and after its adsorption on TiO_2 were measured at different pH solutions. The results were as follows: before the adsorption, pH = 3: COD = 5553 mg/L, pH = 7: COD = 5559 mg/L, pH = 11: COD = 5562 mg/L; after the adsorption, pH = 3: COD = 4957 mg/L, pH = 7: COD = 4369 mg/L, pH = 11: COD = 4802 mg/L. These confirm that there is indeed a maximal adsorption amount of glycerol at pHzpc, which is beneficial to photocatalytic hydrogen evolution.

3.4 Effect of coexisting substances

Because glycerol wastewater comes from soap-making, the fatty acid and biodiesel industry, and some other industrial processes, there are inevitably some coexisting organic compounds and inorganic ions in their wastewater other than glycerol. Thus, we investigated the effect of coexisting methanol, sodium stearate, Cu^{2+}, Fe^{3+} and Fe^{2+} on hydrogen evolution in the presence of glycerol.

As shown in Table 1, methanol enhanced the hydrogen evolution in the glycerol reaction system. This is attributed to the concentration of glycerol being lower than the saturation adsorption concentration, thus methanol could also be adsorbed on TiO_2 as an electron donor which scavenged the photoinduced hole to inhibit the recombination of the photoinduced electron and the hole at the semiconductor surface and the back reaction of H_2 and O_2. Thus, hydrogen evolution rate is promoted.

Sodium stearate markedly decreased the hydrogen evolution rate, which can be attributed to sodium stearate having alkalescence and the pH of glycerol solution becoming about 9 after adding it. Based on the result from 3.3, the pH change of the glycerol solution (from neutrality to alkalescence) markedly decreases the rate. When the solution was adjusted to neutral with H_2SO_4, the rate decreased slightly, which can be attributed to the fact that stearate could compete with glycerol for some adsorption sites on TiO_2, and that it is a weak electron donor for hydrogen evolution.

For metal M, if the potential of the conduction band of TiO_2 is more negative than E^{θ} (M^{n+}/M), the metal ion can be photoreduced [20]. The potential of the conduction band of TiO_2 is -0.3 V(versus NHE at pH = 7), and the E^{θ} (M^{n+}/M) of some metal ions are as follows:

$$E^{\theta}(Cu^{2+}/Cu^{+}) = +0.153\ \mathrm{v},\quad E^{\theta}(Cu^{2+}/Cu) = +0.337\ \mathrm{v}$$
$$E^{\theta}(Fe^{3+}/Fe^{2+}) = +0.771\ \mathrm{v},\quad E^{\theta}(Fe^{2+}/Fe) = -0.440\ \mathrm{v}$$

Thus, Cu^{2+} can be reduced to Cu^{+} or Cu by photoinduced electrons of the conduction band. The TiO_2 surface becomes black red after photocatalytic reaction in glycerol solution containing Cu^{2+}. The deposited species on TiO_2 is a mixture of Cu and Cu_2O [21]. Cu^{2+} not only consumes photoinduced electrons but also poisons the catalyst, thus it decreases the hydrogen evolution rate markedly.

Besides photoreduction of Fe^{3+} to Fe^{2+} by photoinduced electrons, Fe^{3+} can absorb ultraviolet light and the following reactions take place [22,23]:

$$Fe^{3+}_{aq} + H_2O + hv \rightarrow Fe^{2+}_{aq} + H^{+} + OH \qquad (2)$$

$$Fe^{2+}_{aq} + h^{+} \rightarrow Fe^{3+}_{aq} \qquad (3)$$

Because the reaction (3) is homogenous, it should be the main reaction. In these reactions, Fe^{3+} transformed into Fe^{2+} and Fe^{2+} consumed h^{+} to inhibit effectively the combination of the photoinduced electron and the hole, and to enhance the hydrogen evolution rate. Thus, adding Fe^{3+} and Fe^{2+} into the glycerol reaction system increases the rate. In addition, the produced OH can oxidize glycerol.

3.5 Determination of intermediates in liquid phase

To determine intermediates easily, the initial concentration of glycerol was increased by 0.10 mol/L because the concentration of intermediates should also increase. The cyclic voltammetry curves of the reacted solutions were measured under alkaline conditions in the scan potential region of -0.4 to 0.8 V at a rate of 0.08 V/s, and are shown in Fig. 5. Before irradiation, there were only two oxidation peaks, a (strong) and b (medium), for positive scanning, whereas with increase in irradiation time, peak a decreased, and peak b increased before 300 min irradiation and decreased after that time. Peak a can be attributed to the oxidation peak of glycerol, whereas Peak b to the oxidation peak of the oxidized intermediate of glycerol. If glycerol was oxidized by electrochemistry, peak b would decrease with the decrease in peak a. Based on cyclic voltammetry curves, with the increase of irradiation time, peak b increased with peak a, and then decreased after 300 min irradiation. This result demonstrates that glycerol is degraded, and the intermediate increases during the photocatalytic reaction but the intermediate is degraded quickly after 300 min of irradiation.

To confirm the intermediate, we prepared glyceraldehydes through 0.1 mol/L glycerol reacting with H_2O_2 and $FeSO_4$ for 30 min [24], and an electrochemistry analysis

Table 1 Effect of coexisting substances in the glycerol wastewater on initial rate of photocatalytic H_2 generation

Reaction substance	Time/h	$r_{(H2)}$/μ mol/·h^{-1})
0.5 mmol/Lglycerol	0.5	141.42
0.5 mmol/Lglycerol + 0.5 mmol/LCH_3OH	0.5	184.99
0.5 mmol/Lglycerol + 0.5 mmol/L$C_{17}H_{35}COONa$	0.5	105.37
0.5 mmol/Lglycerol + 0.5 mmol/L $CuSO_4$	0.5	84.19
0.5 mmol/Lglycerol + 0.25 mmol/L $Fe_2(SO_4)_3$	0.5	208.41
0.5 mmol/Lglycerol + 0.5 mmol/L $FeSO_4$	0.5	194.10

100 mL solution, natural pH

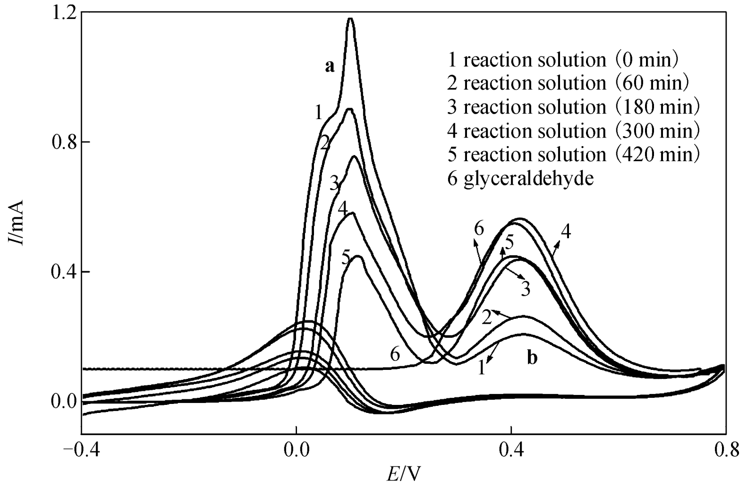

Fig. 5 Cyclic voltammetry patterns of reaction solutions on Pt electrodes

was conducted. As shown in Fig. 5, the peak of glyceraldehyde occurred at the same oxidation potential of the intermediate. This confirms that the intermediate is glyceraldehyde, which is consistent with the report of L. ROQUET [25]. This confirms that glyceraldehyde is formed and degraded after 300 min of irradiation.

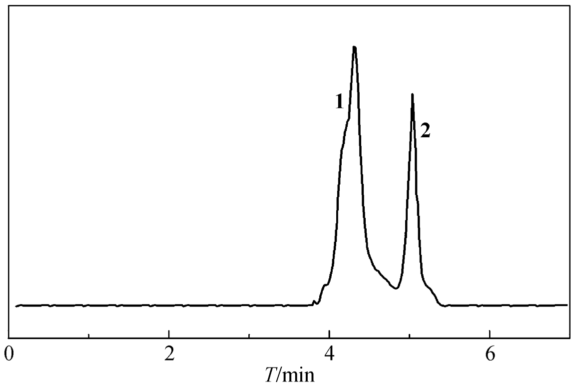

Fig. 6 HPLC pattern of after 3 h photocatalysis degradation of glycerol

The reaction solution was analyzed by HPLC-MS. Figure 6 shows that under the selective working conditions, two peaks occurred in the HPLC pattern. The retention time was 4.35 min for peak **1**, and 5.04 min for peak **2**. These peaks were detected on mass spectra, and the m/z of peaks **1** and **2** are 75 and 59 (molecular ion peak), respectively. These are consistent with the peaks of glycoladehyde and glycolic acid, respectively. Thus, intermediates glycoladehyde and glycolic acid in the reaction solution are identified. In the HPLC pattern, the peak of glyceraldehyde did not occur, which may be attributed to the fact that under the operating conditions for HPLC, glyceraldehyde could not be separated effectively.

In addition, formaldehyde was identified by acetylacetone colorimetry in the reaction solution.

3.6 Discussion of mechanism

Based on the experimental results, the mechanism can be discussed as follows.

The reaction is initiated by the photoexcitation of TiO_2 particles, which leads to the formation of electron-hole pairs. Valence band holes can be filled by the surface hydroxyl groups to form hydroxyl radicals [26].

$$TiO_2 \xrightarrow{hv} h^+ + e_{cb}^- \quad (4)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (5)$$

Pt can trap photogenerated conduction electrons, and the electron acceptor H^+ obtains the electron to produce hydrogen on Pt [18].

$$H^+ + ecb\text{-} \rightarrow 1/2\ H_2 \uparrow /\text{on Pt} \quad (6)$$

Glycerol adsorbed on the catalyst can react with the formed hydroxyl radical:

$$CH_2OHCHOHCH_2OH + \cdot OH \rightarrow CH_2OHCHOHCHOH + H_2O \quad (7)$$

The formed $CH_2OHCHOHCHOH\cdot$ can react with water to form $CH_2OHCHOHCH(OH)_2$ and $H\cdot$ which can transform into H_2 [27] further.

$$CH_2OHCHOHCHOH + H_2O \rightarrow CH_2OHCHOHCH(OH)_2 + H \quad (8)$$

The formed $CH_2OHCHOHCH(OH)_2$ is unstable, which transforms into aldehyde [28] further

$$\begin{aligned}&CH_2OHCHOHCH(OH)_2\\ &\quad \rightarrow CH_2OHCHOHCHO + H_2O\end{aligned} \tag{9}$$

$\cdot OH$ can react continuously with the formed aldehyde:

$$\begin{aligned}&CH_2OHCHOHCHO + OH\\ &\quad \rightarrow CH_2OHCHOHCO + H_2O\end{aligned} \tag{10}$$

$$\begin{aligned}&CH_2OHCHOHCO + H_2O\\ &\quad \rightarrow CH_2OHCHOHCOOH + H\end{aligned} \tag{11}$$

The formed $CH_2OHCHOHCOOH$ can react directly with photoinduced h^+ so that (?) decarboxylation takes place [26].

$$\begin{aligned}&CH_2OHCHOHCOOH + h^+\\ &\quad \rightarrow CH_2OHCHOH + CO_2 + H^+\end{aligned} \tag{12}$$

The formed $CH_2OHCHOH$ repeats the reactions (8), (9), (10), (11) and (12) to form water and carbon dioxide at last.

$CH_2OHCHOH \rightarrow CH_2OHCH(OH)_2 \rightarrow (CH_2OHCHO) \rightarrow CH_2OHCO \rightarrow CH_2OHCOOH \rightarrow CH_2OH \rightarrow HCH(OH)_2$ $(HCHO) \rightarrow HCO \rightarrow HCOOH \rightarrow CO_2 + H_2O$

4 Conclusion

1) Glycerol cannot only improve the efficiency of photocatalytic hydrogen generation but can also be decomposed effectively. Under neutral conditions (at about pH 6.4), the efficiency reaches a maximum.

2) At low concentrations of glycerol, the effect of the concentration on hydrogen evolution is consistent with the Langmuir-Hinshelwood model.

3) Different coexisting substances have different influences on photocatalytic hydrogen generation. Coexisting methanol, Fe^{3+} and Fe^{2+} increase the rate of hydrogen evolution in the glycerol reaction system, whereas sodium stearate and Cu^{2+} markedly decrease the rate.

4) Glycerol degrades through oxidation to continuously form glyceraldehyde, glycoladehyde and glycolic acid, and through decarboxylation, forms CO_2 and H_2O finally.

Acknowledgements The financial support of Department of Sciences and Technology of China (2003CB214503), the National Natural Science Foundation of China (Grant No. 20763006), and the Natural Science Foundation of the Jiangxi Province (No. 2007GZH1754) are gratefully acknowledged.

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