Effects of electrolyte NaCl on photocatalytic hydrogen evolution in the presence of electron donors over Pt/TiO2

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ABSTRACT

The effects of electrolyte NaCl, a major component of natural seawater, on photocatalytic hydrogen evolution in the presence of electron donors over Pt/TiO2 have been investigated. The adsorption performance and surface reaction of electrolyte NaCl and the electron donors on TiO2 have been characterized by electrophoretic analysis and in situ attenuated total reflectance infrared spectroscopy. Under acidic condition Cl^- ions are adsorbed on TiO2, while under neutral and basic condition Na^+ ions are adsorbed on TiO2. In the case of ethanol as an electron donor, the activity of photocatalytic hydrogen evolution over Pt/TiO2 increases when concentration of NaCl < 0.10 mol L^{-1}, while the activity decreases when the concentration > 0.10 mol L^{-1}. At different pH values, the activity decreases in the order: basic > neutral > acidic. In the cases of formic acid and oxalic acid as electron donors, the activities decrease with increase of NaCl concentration. The Na^+ ions can affect adsorption performance of ethanol on TiO2. Possible reaction mechanisms were discussed.

1. Introduction

Photocatalytic splitting water (PSW) using a heterogeneous photocatalyst has been studied extensively as a potential method to supply hydrogen from sunlight and water [1–11]. Although water is abundant on the earth, pure water is scarce because 93% of the earth's water is present in oceans and inland seas and most of the remaining water is isolated as glacier in the Polar Regions [12]. Almost all studies on PWS so far have been performed in pure water (distilled water). From the viewpoint of practical application, producing hydrogen from natural seawater would be highly desirable. Lee et al. reported PWS from seawater over La$_2$Ti$_2$O$_7$ under ultraviolet light, and over CdS/TiO$_2$ under visible light [12]. Domen et al. have investigated effects of some electrolytes including NaCl on the photocatalytic activity of (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) for overall water splitting under visible light ($\lambda > 400$ nm) [13].

In the absence of an electron donor, the efficiency of photocatalytic hydrogen generation is very low because of the recombination of photoinduced electrons and holes on semiconductor surface [14]. In order to achieve higher efficiency for photoinduced hydrogen production, many researches in this field have involved electron donors as sacrificial agents, which can

react irreversibly with the photoinduced holes. From the viewpoint of practical application, the electron donors for the hydrogen generation should be cheap and easy to obtain. We found that photocatalytic hydrogen production increases with simultaneous degradation of pollutants (electron donors) [15–18]. Kondarides et al. have also investigated photocatalytic hydrogen evolution using pollutants as electron donors [19]. Biomass such as glucose, the most versatile renewable resource, has been utilized for photocatalytic hydrogen generation over Pt/TiO$_2$ [20–22], Pt/Cd$_x$Zn$_{1-x}$S [23] and Pt/ZnS–ZnIn$_2$S$_4$ [24]. However, there are few studies on photocatalytic hydrogen production from seawater with pollutants or biomass as electron donors.

The electrophoretic analysis has been widely used to monitor electrolyte adsorption on colloid particles including TiO$_2$ suspension. Attenuated total reflectance (ATR) infrared (IR) spectroscopy is an effective tool to investigate solid/liquid interfacial phenomena, and many literatures have been published recently [16]. In order to understand the surface performances of electrolyte NaCl and organic electron donors on TiO$_2$, electrophoretic analysis and ATR-IR have been used in this work.

Ethanol is a cheap electron donor from biomasses such as starch, and oxalic acid and formic acid are common organic pollutants. In this paper, the effects of electrolyte NaCl on photocatalytic hydrogen evolution in the presence of the electron donors over Pt/TiO$_2$ have been investigated, because NaCl is a major component of natural seawater. Possible reaction mechanisms were discussed.

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2. Experimental

All reagents were of analytical grade and were used without further purification. 0.50 wt% Pt/TiO$_2$ was prepared by the method of photodeposition [15]: 1.00 g anatase TiO$_2$ (Shanghai Kangyu Co. Ltd., particle size 20 nm, BET surface area 124 m^2 g^{-1}), 13.34 mL 1.93×10^{-3} mol L^{-1} H$_2$PtCl$_6$, 1.0 mL anhydrous ethanol and 85.66 mL distilled water were added to a Pyrex cell with a flat window for illumination. Other reaction conditions for Pt deposition were the same as that for photocatalytic hydrogen evolution reaction (see below). After 1 h irradiation, filtration and washing with distilled water, the sample was dried at 393 K for 10 h to obtain 0.50 wt% Pt/TiO$_2$.

Given amounts of the electron donor (formic acid, oxalic acid and ethanol respectively) and NaCl were dissolved into 5.0 mL 0.10 g L^{-1} aqueous TiO$_2$ suspension (prepared by 30 min sonication), and then the suspension was diluted to 50 mL (0.010 g L^{-1} TiO$_2$) with distilled water. The pH of the suspension was adjusted with 0.010 mol L^{-1} HCl or 0.010 mol L^{-1} NaOH, and then sonicated in an ultrasonic bath for 30 min. Zeta potential was measured on a Malvern NANO ZS90 Zetasizer. To determine the zero point of charge of the TiO$_2$, the same concentration suspension of TiO$_2$ was used.

Infrared absorption spectra were measured on a BRUKER TENSOR 37 FT-IR spectrometer equipped with a ZnSe crystal horizontal unit. Aqueous suspensions of TiO$_2$ were prepared as follows. 0.10 g TiO$_2$ was added to 10 mL solution containing NaCl and ethanol, and then the mixture was dispersed for 30 min in an ultrasonic bath. 50 μL of the suspension was added onto the surface of the ZnSe crystal. After standing for 20 s to deposit TiO$_2$, the measurement was conducted. All spectra were obtained from 500 scans at a resolution of 4 cm^{-1}.

The photocatalytic reaction was carried out in a Pyrex flask of 190 mL with a flat window at room temperature. 0.050 g photocatalyst and 100 mL solution containing the electron donor and NaCl were added to the cell. The reaction mixture inside the cell was maintained in suspension by means of magnetic stirring. A 400 W high pressure Hg lamp was used as the light source. A water-cooling jacket outside the lamp was used to remove the IR fraction of the beam. The UV incident light intensity (λ: 320–400 nm) was 2.52 mW cm^{-2}, determined by a UV-A radiometer. Prior to irradiation, suspension of the catalyst was dispersed in an ultrasonic bath for 1 min and nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen. The top of the cell was sealed with a silicone rubber septum. Sampling was made intermittently through the septum during experiments. The amount of photocatalytic hydrogen evolution for 1 h irradiation was determined on a gas chromatograph (TCD, 13 X column, nitrogen as carrier gas).

3. Results and discussion

3.1. Surface performances of electron donors and NaCl on TiO$_2$

Fig. 1 shows effect of NaCl concentration on zeta potential of TiO$_2$ in the presence of formic acid and oxalic acid. With increase of NaCl concentration, zeta potential of TiO$_2$ in the presence of formic acid decreases (from 26.50 mV to 9.38), while the potential in the presence of oxalic acid increases (from −29.13 mV to ca. 0). At high NaCl concentration (above 0.50 mol L^{-1}), their zeta potentials are almost independent of the NaCl concentration.

In water solution, there are many surface hydroxyl groups on TiO$_2$ [25] and the superficial ionization equilibriums of TiO$_2$ can be expressed by
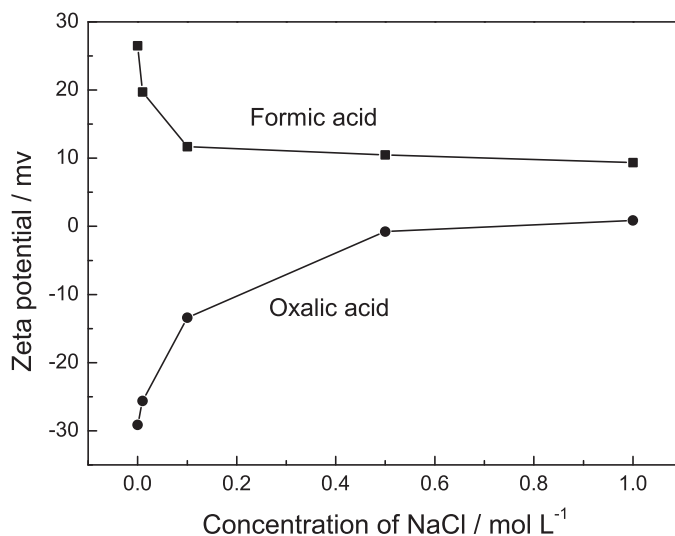
$$> \text{TiOH}_2^+ \xleftrightarrow{K_{a1}} > \text{TiOH} + \text{H}^+ \tag{1}$$

Fig. 1. Zeta potentials of TiO$_2$ at different NaCl concentrations in the presence of 1.0×10^{-2} mol L^{-1} formic acid and 1.0×10^{-2} mol L^{-1} oxalic acid.

$$> \text{TiOH} \xleftrightarrow{K_{a2}} > \text{TiO}^- + \text{H}^+ \tag{2}$$
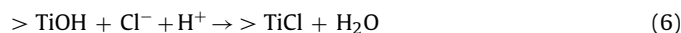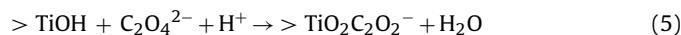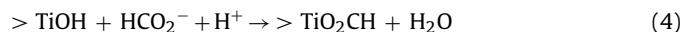
where >TiOH represents the "titanol" surface group. K_{a1} is acidity constant for the first dissociation of Eq. (1), and K_{a2} is acidity constant for the second dissociation of Eq. (2). The pH of zero point of charge, pHzpc, is given by one half of the sum of two surface pK_a's (negative log of the acidity constants) as follows:

$$\text{pHzpc} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2}) \tag{3}$$

In the case of Degussa P25, the corresponding surface acidity constants were found to be pK_{a1} = 4.5, pK_{a2} = 8.0, which yield a pHzpc = 6.25 [25]. In the case of the used TiO$_2$ in this work, pHzpc was determined to be 4.77 by the electrophoretic analysis.

HCO$_2^-$, C$_2$O$_4^{2-}$ and Cl$^-$ ions in aqueous solution undergo inner-sphere ligand substitution reactions with surface of TiO$_2$ as follows [16,25]:

$$> \text{TiOH} + \text{HCO}_2^- + \text{H}^+ \rightarrow > \text{TiO}_2\text{CH} + \text{H}_2\text{O} \tag{4}$$

$$> \text{TiOH} + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow > \text{TiO}_2\text{C}_2\text{O}_2^- + \text{H}_2\text{O} \tag{5}$$

$$> \text{TiOH} + \text{Cl}^- + \text{H}^+ \rightarrow > \text{TiCl} + \text{H}_2\text{O} \tag{6}$$

Acidic condition is favorable for these reactions. In addition, because formate and oxalate are bidentate ligands [16], they should be adsorbed on TiO$_2$ surface more strongly than Cl$^-$.

The electric double layer model can be employed for TiO$_2$–electrolyte–water interface to provide a quantitative understanding of processes such as surface-charge development, adsorption of aqueous ions onto the oxide surface. In the case of formic acid (pK_a: 3.77), the surface hydroxyl groups exist mainly in >TiOH$_2^+$ and >TiOH, and a part of the groups transfer into >TiO$_2$CH species (uncharged) as shown in reaction (4). Thus, the zeta potential without NaCl is positive. With addition of NaCl, reaction (6) takes place and counter Cl$^-$ ions enter the stern layer (compact layer) of TiO$_2$ particles. Thus, the zeta potential decreases with increase of NaCl concentration. In the case of oxalic acid, the amount of >TiO$_2$C$_2$O$_2^-$ (negative charged) should be larger than that of >TiOH$_2^+$, because the zeta potential without NaCl is negative. With addition of NaCl, reaction (6) can also take place due to a large amount of H$^+$ (pK_a: 1.25) ions in the solution. However, because net surface charge of TiO$_2$ is negative and oxalate is a stronger chelating ligand than formate, reaction (6) should take place more difficultly in oxalic acid system than in formic acid system. With addition of
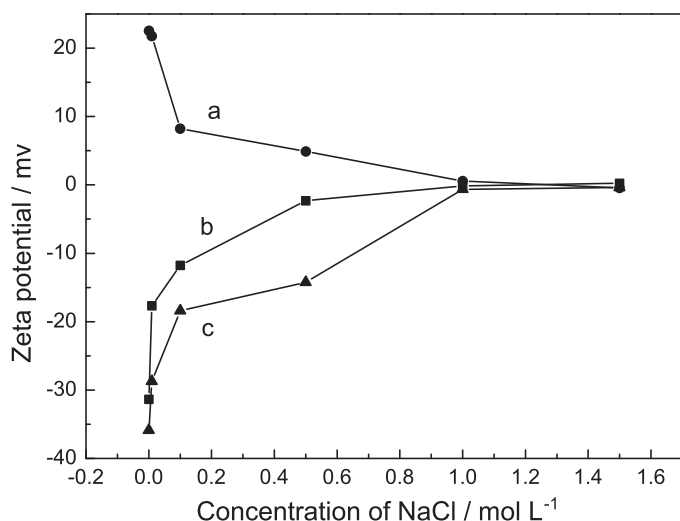
Fig. 2. Zeta potentials of TiO_2 at different NaCl concentration and different pH values in the presence of 1.7×10^{-1} mol L^{-1} ethanol (1.0 mL ethanol in 100 mL solution). (a) pH 3.82 (1.0×10^{-4} mol L^{-1} HCl), (b) pH 6.34 (natural pH) and (c) pH 9.58 (1.0×10^{-4} mol L^{-1} NaOH).

NaCl, counter Na^+ ions enter the stern layer of TiO_2 particles. Thus, the zeta potential increases with increase of NaCl concentration.

Because ethanol molecule is electroneutral, the surface charge of TiO_2 depends only on the acid–base equilibriums. Fig. 2 presents effect of NaCl concentration on zeta potential of TiO_2 at different pH values in the presence of ethanol. Under acid condition (pH < pHzpc), the zeta potential of TiO_2 without NaCl is positive. With increase of NaCl concentration, the zeta potential decreases and then reaches a plateau (curve a). Cl^- ions should be adsorbed on TiO_2 by reaction (6). Because H^+ concentration (1.0×10^{-4} mol L^{-1} HCl) in this system is much lower than in formic acid system (pH: 2.78), the reaction degree of reaction (6) in the ethanol system is lower than in the formic acid. Under the neutral and basic condition (pH > pHzpc), the zeta potential of TiO_2 without NaCl is negative. With increase of NaCl concentration, the zeta potential increases and then reaches a plateau (curves b and c). Na^+ cation can form inner-sphere complex with the surface functional groups and/or the chemisorbed water molecules on anatase TiO_2 [26]. Thus, under neutral and basic condition, the adsorption of Na^+ can be expressed as follows:

$$> TiO^- + Na^+ \rightarrow\, > TiONa \tag{7}$$

The more there are $>TiO^-$ species, the more $>TiONa$ species can be formed with increase of NaCl concentration.

Ethanol can be adsorbed on TiO_2 by hydrogen bond. Because the ethyl of ethanol is an electron-donating group, the formed hydrogen bond by the hydroxyl of ethanol on TiO_2 is weak. Na^+ can form complex with ethanol by oxygen of the hydroxyl [27]. When Na^+ forms complex with ethanol as shown in Scheme 1, the strength of hydrogen bond by the ethanol hydroxyl on TiO_2 will enhance due to electron withdrawing of Na^+. When pH > pHzpc, Na^+ ions can be adsorbed on TiO_2. With increase of NaCl concentration, due to increasing of $>TiONa$ species, more ethanol molecules can be adsorbed on TiO_2 via the stronger hydrogen bond.

Fig. 3 presents infrared spectra of ethanol adsorbed on TiO_2 at pH 9.58 and different NaCl concentrations. The absorption peaks are very small, indicating that the adsorption of ethanol on TiO_2 is very weak, because adsorption affinity via hydrogen bond is very weak. The bands at 1045 cm^{-1} and 1084–1089 cm^{-1} can be assigned to ν O–C and ν C–C vibrations, respectively [28,29]. Without ethanol, no bands can be observed (curve a). A control experiment showed the absorption bands of aqueous ethanol without TiO_2 occurred at
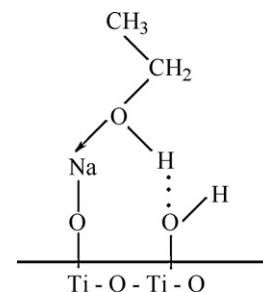
Scheme 1. Schematic illustration of the interaction between Na^+ ion adsorbed and ethanol molecule adsorbed on TiO_2 via hydrogen bond.

1045 cm^{-1} and 1090 cm^{-1}. Comparing curve b with curve c and d in Fig. 3, one can observes that in the presence of NaCl, the ν C–C absorption band shifts towards low wavenumber (from 1089 to 1084 cm^{-1}). This indicates that adsorbed Na^+ can affect the adsorption performance of ethanol on TiO_2. Because the adsorption amount of ethanol on TiO_2 would be very small and there were a large experimental error, one could not observe increase of the intensity of the IR peaks in the presence of NaCl in solution.

In aqueous solution, the interaction between Na^+ and ethanol is very weak because amount of water molecules is much larger than that of ethanol molecules. When Na^+ ions are adsorbed on TiO_2, relative concentration of Na^+ on TiO_2 (compared to that in the bulk solution) would increase. This would result in enhancement of the interaction between adsorbed Na^+ and ethanol as shown in Scheme 1. Because of Na^+ being electron withdrawing, strength of the bond C–C should decrease. Under the basic condition (pH > pHzpc), $>TiONa$ species forms in the presence of NaCl. As a result, the absorption band (ν C–C) shifts towards lower wavenumber. This confirms indirectly that Na^+ adsorbed on TiO_2 can increase hydrogen bond strength between the ethanol molecule and surface hydroxyl (Scheme 1).

3.2. Photocatalytic hydrogen evolution at different NaCl concentrations in the presence of electron donors

Fig. 4 presents photocatalytic hydrogen evolution at different NaCl concentrations in the presence of formic acid and oxalic acid over Pt/TiO_2. With increase of NaCl concentration, the activities for the hydrogen evolution decrease in both oxalic acid and formic
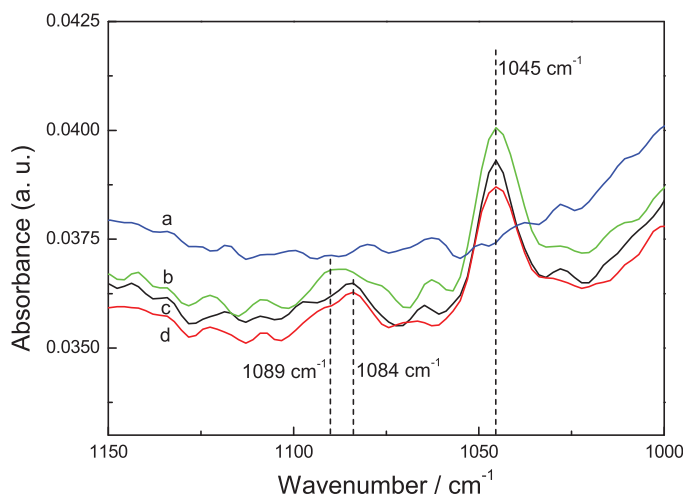

Fig. 3. Infrared spectra of ethanol adsorbed on TiO_2 at pH 9.58 and different NaCl concentrations in the presence of 1.7×10^{-1} mol L^{-1} ethanol. Concentrations of NaCl are 0 (b), 1.0×10^{-1} (c) and 1.0 mol L^{-1} (d), respectively. Curve a is spectrum of aqueous TiO_2 suspension without ethanol.

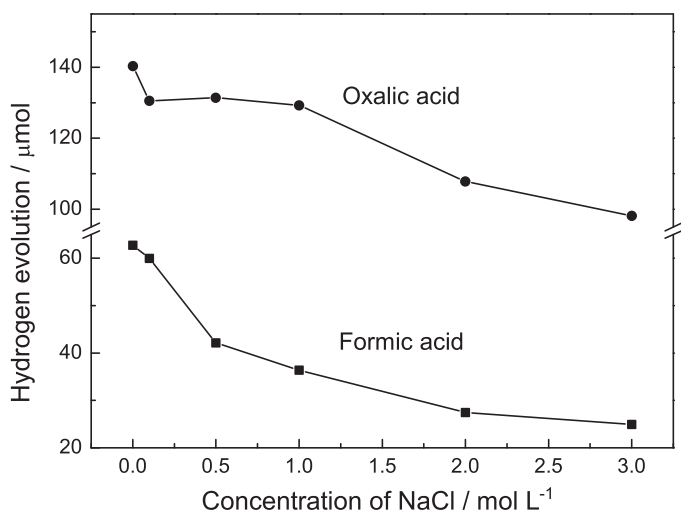**Fig. 4.** Photocatalytic hydrogen evolution at different NaCl concentrations in the presence of 1.0×10^{-2} mol L^{-1} formic acid and 1.0×10^{-2} mol L^{-1} oxalic acid over Pt/TiO$_2$. Conditions: 100 mL solution, natural pH, 0.050 g 0.50 wt% Pt/TiO$_2$, 1 h irradiation.

acid system. In the case of formic acid, the activity decreases by 60% at 3.0 mol L^{-1} NaCl, while that decreases by 30% in the case of oxalic acid. In formic acid system, lower NaCl concentration decreases markedly H$_2$ production, whereas higher NaCl concentration decreases slightly. However, in oxalic acid system, lower NaCl concentration decreases slightly H$_2$ production, whereas higher NaCl concentration decreases notably.

The inhibitory effect of chloride ion on the photocatalytic pollutant degradation has been reported [30]. The inhibiting effect is due to the hole scavenging properties of chloride ion.

$$Cl^- + h^+ \rightarrow {}^\bullet Cl \tag{8}$$

However, we cannot observe photoreduced product of Cl$_2$ in gas phase (determining by mass spectrometry) and Cl$_2$ or HOCl species in the reacted solution (determining by adding KI-starch solution to the reacted solution). This could be attributed to the formed $^\bullet$Cl being reduced by the conduction electron:

$$^\bullet Cl + {}^\bullet e_{cb}^- \rightarrow Cl^- \tag{9}$$

As a result, the adsorbed Cl$^-$ ions (>TiCl species) should decrease the photocatalytic activity. As shown in Fig. 1, when NaCl concentration is lower, reaction (6) should take place effectively in formic acid system, whereas Na$^+$ ions but not Cl$^-$ ions were adsorbed on TiO$_2$ in oxalic acid system due to negative surface charge of TiO$_2$. Thus, lower NaCl concentration affects markedly H$_2$ production in formic acid system but not in oxalic acid system. When NaCl concentration is higher, the adsorption of Cl$^-$ ions on TiO$_2$ would near saturation in formic acid system, and the Cl$^-$ ions could be adsorbed markedly in oxalic acid system. As a result, higher NaCl concentration decreases markedly H$_2$ production in oxalic acid system but not in formic acid system. Because more Cl$^-$ ions are adsorbed on TiO$_2$ in formic acid solution than those in oxalic acid solution (Fig. 1), the activity in formic acid system decreases more than that in oxalic acid system.

Fig. 5A and B shows time courses of photocatalytic hydrogen evolution over Pt/TiO$_2$ at different NaCl concentrations in the presence of formic acid and oxalic acid, respectively. With increase of NaCl concentration, the activities of photocatalytic hydrogen evolution decrease in both formic acid and oxalic acid system, in agreement with the result from Fig. 4. NaCl can affect more markedly the hydrogen evolution in formic acid system (Fig. 5A)
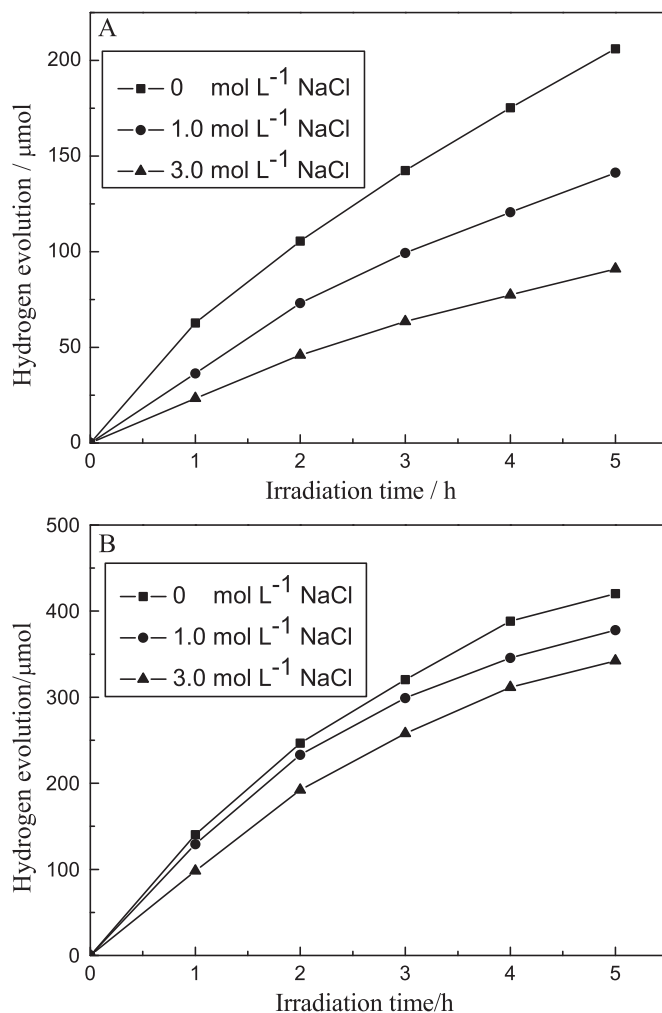

Fig. 5. Time courses of photocatalytic hydrogen evolution at different NaCl concentrations in the presence of 1.0×10^{-2} mol L^{-1} formic acid (A) and 1.0×10^{-2} mol L^{-1} oxalic acid (B). Conditions: 100 mL solution, natural pH, 0.050 g 0.50 wt% Pt/TiO$_2$.

than in oxalic acid system (Fig. 5B), which is similar to the case of Fig. 4.

Fig. 6 shows photocatalytic hydrogen evolution at different NaCl concentrations and different pH values in the presence of ethanol over Pt/TiO$_2$. Under basic and neutral condition (curve c and b), the photocatalytic activities increases with NaCl concentration to a maximum at 0.10 mol L^{-1} NaCl, beyond which the photocatalytic activities decrease. It is interesting that the enhancement of the activity under basic condition is larger than that under neutral condition. Under acidic condition (curve a), the activity decreases with increase of NaCl concentration, which is similar to the results in oxalic acid and formic acid system.

Under basic and neutral condition, because Na$^+$ can form complex with adsorbed ethanol (Scheme 1), the enhancement of hydrogen bond strength between the adsorbed ethanol and surface hydroxyl is beneficial to the ethanol trapping photoinduced hydroxyl radical or hole [16]. This leads to increasing the photocatalytic activity. Because more Na$^+$ ions adsorbed on TiO$_2$ under basic condition than under neutral condition, enhancement of the activity under basic condition is larger than that under neutral condition. At high NaCl concentration, hydration of the TiO$_2$ interface is not complete (surface reactant H$_2$O being not enough) and viscosity of the solution increases (low diffusion rate for reactants in the bulk solution and interface) [31]. These would result in decreasing the activities under neutral and basic condition.
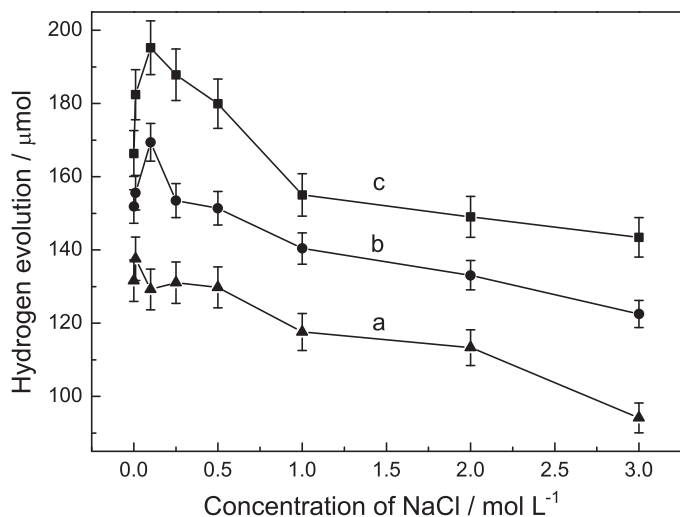
Fig. 6. Photocatalytic hydrogen evolution at different NaCl concentrations and different pH values in the presence of 1.7×10^{-1} mol L^{-1} ethanol over Pt/TiO$_2$. (a) pH 3.82, (b) pH 6.34 (natural pH) and (c) pH 9.58. Other conditions as in Fig. 5.

Under acidic condition, Cl$^-$ ions can be adsorbed on TiO$_2$. Thus, the same effect in oxalic acid and formic acid system should occur in the ethanol system. But in the ethanol system, because H$^+$ concentration (1.0×10^{-4} mol L^{-1} HCl) is much lower than those in the formic acid system, the amount of reacted Cl$^-$ ions via reaction (6) is lower. As a result, the activity decreases more slowly than that in the formic acid system with increase of NaCl concentration (comparing Fig. 6 with Fig. 4).

Fig. 7 presents time courses of photocatalytic hydrogen evolution over Pt/TiO$_2$ at different NaCl concentrations in the presence of ethanol at pH 9.58. The activity of photocatalytic hydrogen evolution at different NaCl concentrations decreases in the order: 0.10 mol L^{-1} > 0 mol L^{-1} > 3.0 mol L^{-1}, in agreement with the result from Fig. 6.

Fig. 8 shows time courses of photocatalytic hydrogen evolution over Pt/TiO$_2$ at different ethanol concentrations in the presence of 1.0×10^{-1} mol L^{-1} NaCl. With increase of ethanol concentrations, the activity of photocatalytic hydrogen evolution increases. However, when ethanol concentration >1.7×10^{-1} mol L^{-1}, the activity does not increase markedly. This would be due to the amount of

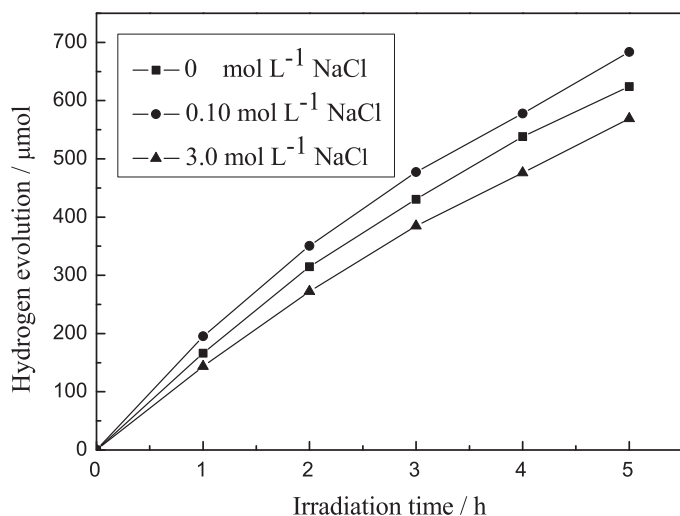**Fig. 7.** Time courses of photocatalytic hydrogen evolution at different NaCl concentrations in the presence of 1.7×10^{-1} mol L^{-1} ethanol. Conditions as in Fig. 5 except pH 9.58.
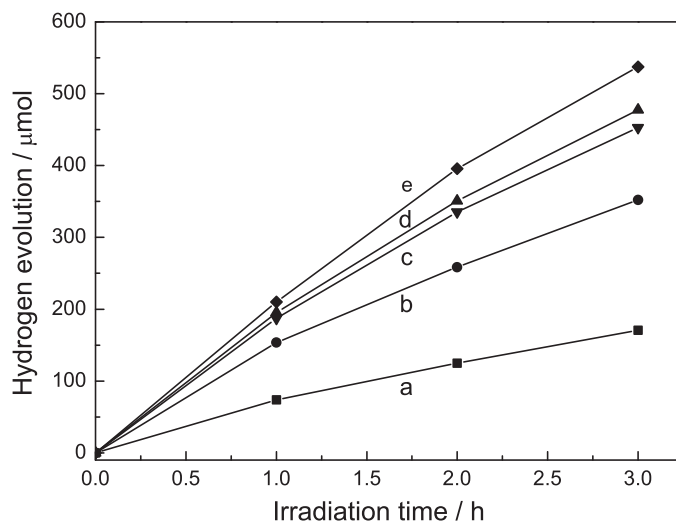

Fig. 8. Time courses of photocatalytic hydrogen evolution at different ethanol concentrations in the presence of 1.0×10^{-1} mol L^{-1} NaCl. Ethanol concentrations are 0.010 (a), 0.10 (b), 0.17 (c), 0.50 (d) and 1.0 mol L^{-1}(e), respectively. Conditions as in Fig. 5 except pH 9.58.

ethanol adsorbed at >TiONa sites (Scheme 1) nearing saturation when ethanol concentration is higher.

4. Conclusions

The effects of electrolyte NaCl on photocatalytic hydrogen evolution in the presence of the electron donors over Pt/TiO$_2$ have been investigated. Under acidic condition Cl$^-$ ions are adsorbed on TiO$_2$, while under neutral and basic condition Na$^+$ ions are adsorbed on TiO$_2$. In the case of ethanol as an electron donor, the activity of photocatalytic hydrogen evolution increases when NaCl < 0.10 mol L^{-1}, while the activity decreases when NaCl > 0.10 mol L^{-1}. At different pH values, the activity decreases in the order: basic > neutral > acidic. Na$^+$ adsorbed on TiO$_2$ under basic condition can enhance hydrogen bond strength between adsorbed ethanol and the surface hydroxyl, which is beneficial to the hydrogen evolution. In the cases of formic acid and oxalic acid as electron donors, the activities decrease with increase of NaCl concentration, which is due to the effect of adsorbed Cl$^-$ ions.

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