Electrochemically promoted photocatalytic oxidation of nitrite ion by using rutile form of TiO_2/Ti electrode

Chih-Cheng Sun [a], Tse-Chuan Chou [b],[*]

[a] *Department of Chemical Engineering, Yung-Ta Industrial Commercial College, Pingtung 909, Taiwan*
[b] *Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan*

Abstract

The photocatalytic oxidation of nitrite ion in a NaCl aqueous solution using the rutile form of TiO_2/Ti as the working electrode was studied. Experimental results indicate that the rutile form of TiO_2/Ti film electrode has excellent photoactivity by applying a bias potential and irradiation simultaneously. The incident photo-to-current conversion efficiency (IPCE) of this working electrode is a function of the applying bias potential. The photocurrent efficiency of nitrite ion oxidation was 33–40% at a pH of about 7. The oxidation rate of the nitrite ion in brine wastewater using the rutile form of TiO_2/Ti electrode can be estimated by photocurrent measurements. The applying bias potential, light power and pH value were the major factors affecting the oxidation rate and the photocurrent efficiency of nitrite ion oxidation, while the concentrations of nitrite ion was minor. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic; Nitrite ion; Photocurrent efficiency; Photoelectrochemical oxidation; Titanium dioxide

1. Introduction

A photocatalytic process with a redox activity from light-excited electrons and holes was recognized as an useful method for the detoxification of pollutants in both air and water [1–4]. The photocatalytic reaction has been studied since the discovery of photolysis of water using TiO_2 as a photocatalyst [5]. Recently, the applications of photocatalytic techniques have been extensively discussed [6–11].

TiO_2 is the most attractive photocatalyst for decreasing pollutants and purifying both water and air [6,12,13]. For the oxidation of pollutants in aqueous streams, numerous investigations have attempted to develop the supported TiO_2 film catalyst [7–11,14,15]. The photocatalytic reaction on the TiO_2 film electrode was studied [10,11,14,15], and the TiO_2 film supported by a conductive material exhibits interesting photoelectrochemical properties. For a TiO_2 film coated electrode, the anatase form is the commonly used photocatalyst [16], but the rutile form of TiO_2 is recognized as

* Corresponding author. Tel.: +886-6-2757575 ext. 62639; fax: +886-6-2366836; E-mail: tcchou@mail.ncku.edu.tw

photocatalytic inactive material. In order to maintain the anatase form of TiO_2 film, the calcination temperature of the TiO_2 film is held lower than 500°C for the preparation of a TiO_2 film coated electrode [17]. However, the adhesion of the anatase form of TiO_2 films and the phenomena of applying high bias potential on these film electrodes has seldom been mentioned. In general, increasing the calcination temperature increases the adhesion of the TiO_2 film onto the substrate [17,18]. The adhesion of the rutile form of TiO_2 film onto the Ti substrate may be better than that of the anatase form. For the practice view, the adhesion of TiO_2 film is significant to endure bias potential, especially high bias potential, in electrochemically assisted photocatalytic reaction. However, no or a few reports concerning the rutile form of TiO_2 film electrode have been found. A photoelectrochemical reaction by applying a bias potential on the rutile form of a TiO_2 coated film electrode is interesting.

The supporting electrolytes of this photoelectrochemical system, such as H_2SO_4, $NaClO_4$, Na_2SO_4 and NaOH, in an aqueous solution have been reported in literature [18–21]. However, the photoelectrochemical reactions of organic and inorganic species in 1–3% NaCl solution have rarely been mentioned [21]. For example, the photoelectrochemical oxidation of nitrite ion in aquatic breeding water using supported TiO_2 film photoelectrode is unclear.

The nitrite ion is a toxic material usually formed in wastewater or in fish breeding water [22–24]. The nitrite ion is a seriously toxic material even at extremely low concentrations, particularly in aquatic breeding water [23,24]. Previous investigators have examined the feasibility of oxidizing nitrite ion by supplying oxygen in an aqueous solution using different semiconductor powders as photocatalysts [25–27]. They reported that the nitrite ion could be decomposed by a suspension photocatalyst in the presence of oxygen. The oxidation of nitrite ion in a $NaClO_4$ solution using an anatase form of a TiO_2 film electrode by applying a low bias potential was reported [19]. But a photocatalytic reaction of nitrite ion oxidation using the rutile form of TiO_2 film electrode by applying high electric field was not found. In addition, the detoxication of nitrite ion in brine, which contains 1–3% NaCl, is significant in aquaculture. Furthermore, the photocurrent efficiency of the photoelectrochemical oxidation of nitrite ion using a rutile form of TiO_2 film electrode in a NaCl solution is unclear.

In this work, the photoelectrochemical oxidation of nitrite ion in a NaCl aqueous solution using the rutile form of a TiO_2/Ti film electrode was systematically studied. The effect of light power, applying bias potential and pH value on both the reaction rate and photocurrent efficiency of nitrite ion oxidation were also studied.

2. Experimental

2.1. Preparing TiO_2 / Ti electrode

A Ti plate with a 30-cm^2 surface area was etched by a 18-M of hydrogen chloride at 90°C for 2 h and then washed with distilled water in an ultrasonic bath. The treated Ti plate was dried in an oven at 100°C for 30 min, and then immersed in a suspension solution containing 2.00 g of TiO_2 (Degussa P25) in a 20 ml 10% $TiCl_4$ and 90% ethanol. The coated TiO_2 film was dried at a constant moisture air, then, calcinated at 650°C for 2 h. Finally, the structure of the TiO_2 coated plate was analyzed by X-ray diffractometer (Rigaku D/max III V XRD). The applied current and voltage of the X-ray diffraction (XRD) were 30 mA and 40 kV, respectively. During the analysis, the sample was scanned from 20° to 80° at a speed of 0.4°/min.

2.2. Measurement of current on TiO_2/Ti electrode

The desired NaCl concentration and volume of the electrolyte were prepared and added into the divided cell. The prepared TiO_2/Ti plate was used as the working electrode, and a platinum electrode with a 4.50 cm^2 surface area was used as a counter electrode. The experimental apparatus set up was described previously [28]. The current was measured by applying a bias potential and irradiation simultaneously on the working electrode, and was recorded by an EG & G 273A Potentiostat/Galvanostat with a 270 Electrochemical Analysis System. All potentials were specified to the reference electrode, Ag/AgCl/saturated KCl aqueous solution, prepared in our laboratory. The irradiation light was supplied by a supper-high-pressure Hg(Xe) lamp (Oriel) which was operated at different powers by adjusting power supply output.

2.3. Photoelectrochemical oxidation of nitrite ion

The desired nitrite ion concentration was added into a 200-ml 1–3% NaCl electrolyte, which was deoxygenated by nitrogen gas in the reactor. This reactor is the same used for the current measurements. The photocatalytic oxidation of nitrite ion was carried out by simultaneously applying both irradiation and a bias potential. Samples were periodically taken with a pipette from the reactor and then analyzed. According to the APHA testing method [29], the nitrite ion concentration was determined by a Jasco UV–Vis spectrophotometer (Jasco) at a wavelength of 543 nm, a color reagent was added to the sample by the *N*-1-naphthyl ethylene diamine dihydrochloride (NEDA) colorimetric method. The pH values were determined using a pH meter.

2.4. Photocurrent efficiency of nitrite ion oxidation

The photocurrent efficiency of nitrite ion photoelectrochemical oxidation (η) is defined as

$$\eta = \frac{(\text{Mole of nitrite ion oxidized during a period of a run}) \times 2}{(\text{Faraday's of photocurrent passed during the same period of a run})}$$

$$\eta = \frac{2([NO_2^-]_o - [NO_2^-]_t)V_1}{(I_p t)/96{,}500} \tag{1}$$

Where $[NO_2^-]_0$ and $[NO_2^-]_t$ are the nitrite ion concentrations at the initial time and time t, respectively. I_p is the photocurrent, and V_1 is the volume of reaction solution. The η value is based on the photocurrent measured from the TiO_2/Ti electrode, and it differs from the IPCE which is based on the incident photon [30]. The oxidized nitrite ion could be calculated from the analysis of the nitrite ion concentration in the solution. The number ''2'' of the multiplier in the numerator of Eq. (1) represents 2 mol of hole required to oxidize 1 mol of nitrite ion in photoelectrochemical oxidation.

3. Results

3.1. Properties of TiO_2/Ti electrode

Fig. 1 shows the XRD spectra of the Ti plate, TiO_2 powder (Degussa P25) and TiO_2 film on the titanium plate calcinated at 650°C. The peaks at $2\theta = 25.5°$ and $48.0°$ in the spectrum of TiO_2 are
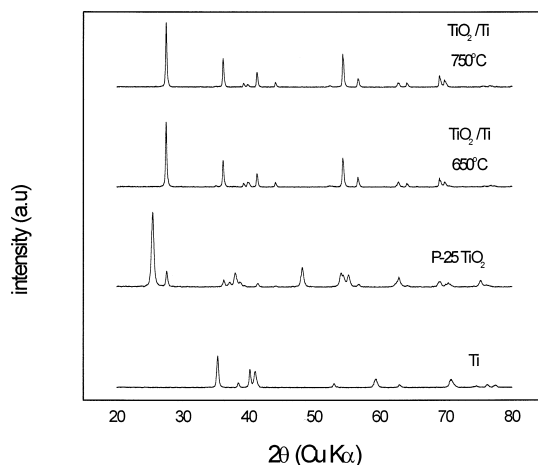
Fig. 1. XRD spectra of Ti plate, TiO_2 powder (Degussa P25) and TiO_2/Ti electrode.

easily identified as the crystal of anatase form, whereas the crystal peaks at $2\theta = 27.6°$ and $54.5°$ are also easily identified as the crystal of rutile form. After the TiO_2 coated Ti plate was calcinated at 650°C, the adhesion of TiO_2 film on the Ti plate is fine, and the peak of the anatase form disappears, only the peak of rutile form remains. It indicates that all of the crystals on this TiO_2 coated film electrode transfer from the anatase to the rutile form. In order to maintain fine adhesion of TiO_2 film on the Ti plate, the calcination temperature higher than 650°C is needed in our manufacturing procedure.

3.2. Photoelectrochemical properties of TiO_2 / Ti electrode

Fig. 2 shows that increasing the applying bias potential from 0.00 to 4.00 V (vs. Ag/AgCl) increases the current density from 0.34 to 2.65 mA/cm^2 under irradiation on the TiO_2/Ti electrode
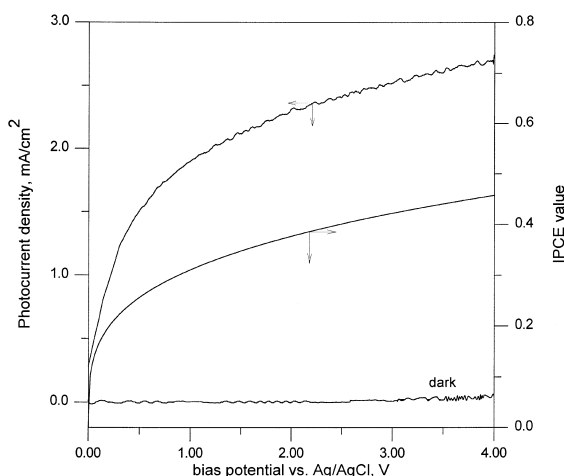

Fig. 2. Effect of applying bias potential on both the photocurrent density and IPCE. Working electrode, 7.06 cm^2 TiO_2/Ti; counter electrode, 4.5 cm^2 Pt; temperature, 30°C; agitation rate, 250 rpm; potential vs. Ag/AgCl; electrolyte, 0.51 M NaCl, pH = 5.50; light power, 400 W.

in a 0.51-M NaCl solution. Without irradiation on this TiO$_2$/Ti electrode, no current, i.e., dark current, was measured by applying bias potential in a range from 0.00 to 4.00 V as shown in Fig. 2. In this electrochemically promoted photocatalysis, the current was contributed from the TiO$_2$ photocatalyst on the TiO$_2$/Ti electrode, the TiO$_2$ was excited by the incident photons. Because no dark current occurred, the current measured from the TiO$_2$/Ti electrode can be considered as photocurrent, even at high application potential on the TiO$_2$/Ti electrode.

The photoelectrochemical property of a photocatalytic electrode is generally determined by the incident photo-to-current conversion efficiency (IPCE) [30–34].

$$IPCE = \iota hc / \lambda Pe \tag{2}$$

where ι is the photocurrent density, h is Planck's constant, c is the velocity of light, λ is the wavelength, P is the light power density and e is the element charge. Fig. 2 also indicates that the IPCE value increases from 5 to 45% when the applying bias potential increases from 0.00 to 4.00 V (vs. Ag/AgCl). Based on the results of the photocurrent density and IPCE values, it can be displayed that the applying bias potential promotes the photoactivity of the rutile form of TiO$_2$ photocatalyst, which is recognized as photon inactive material in suspension system in the absence of oxygen, and the photocurrent efficiency (IPCE) is enhanced by the bias potential.

3.3. Preliminary test of nitrite ion oxidation

To investigate the photocatalytic activity of the rutile form of TiO$_2$/Ti electrode in this electro-chemically promoted system, the photoelectrochemical oxidation of nitrite ion using the applying bias potential was carried out. Fig. 3 summarizes the results of the photoelectrochemical oxidation of nitrite ion in a 0.51-M NaCl aqueous solution. The results indicate that (a) no nitrite ion oxidation occurs under irradiation for 30 min in the absence of a TiO$_2$ film electrode, (b) without applying bias potential, the photooxidation rates of nitrite ion was 1.95 μmol/(l min) with an oxygen supply on the TiO$_2$/Ti electrode, (c) by increasing the applying bias potential from -0.20 to 2.00 V (vs.
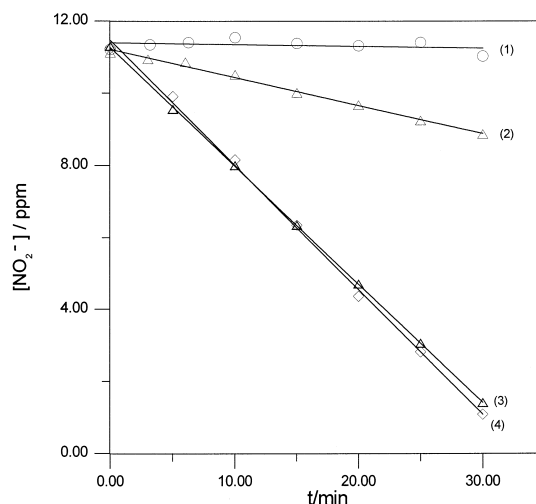

Fig. 3. Nitrite ion concentration as a function of irradiation time in photocatalytic reaction. Initial nitrite ion concentration, 10 ppm; temperature, 30°C; agitation rate, 250 rpm; electrolyte, 0.51 M NaCl, pH = 5.50; light power, 400 W. (1) Without TiO$_2$/Ti photoelectrode, with O$_2$ supply; (2) with TiO$_2$/Ti and O$_2$ supply, without applying bias potential; (3) with 2.00 V (vs. Ag/AgCl) bias potential and O$_2$ supply; (4) with 2.00 V (vs. Ag/AgCl) bias potential, without O$_2$ supply.
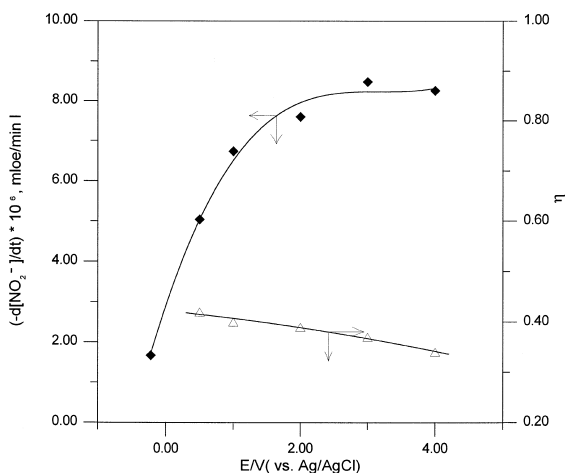
Fig. 4. Effect of applying bias potential on both the initial reaction rate and the photocurrent efficiency of nitrite ion oxidation. Initial nitrite ion concentration, 20 ppm; temperature, 30°C; agitation rate, 250 rpm; electrolyte, 0.51 M NaCl, pH = 5.50; light power, 400 W.

Ag/AgCl), the photoelectrochemical oxidation rate of nitrite ion was increased from 1.95 to 7.60 μmol/(l min) whatever an oxygen supply. Experimental results reveal that the applying bias potential significantly promoted the photocatalytic activity of the rutile form of TiO_2/Ti electrode and increased the reaction rate of nitrite ion oxidation.

3.4. Effect of applying bias potential

Increasing the applying bias potential from 0.00 to 2.00 V (vs. Ag/AgCl), the reaction rate of nitrite ion oxidation increased from 3.05 to 7.60 μmol/(l min). Further increasing the bias potential from 2.00 to 4.00 V, the reaction rate increased slowly from 7.60 to 8.10 μmol/(l min) as shown in Fig. 4. The applying bias potential significantly promotes the reaction rate, but it has a limitation of
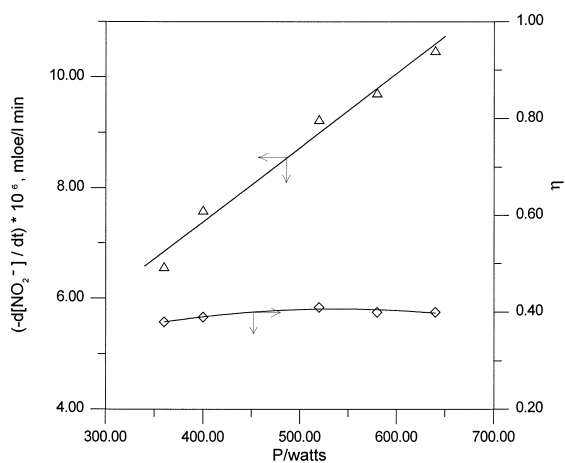

Fig. 5. Effect of light power on both the initial reaction rate and the photocurrent efficiency of nitrite ion oxidation. Initial nitrite ion concentration, 20 ppm; temperature, 30°C; agitation rate, 250 rpm; potential, 2.00 vs. Ag/AgCl; electrolyte, 0.51 M NaCl, pH = 5.50.

promotion when the applying bias potential is higher than 2.00 V (vs. Ag/AgCl). In addition, Fig. 4 also shows that increasing the applying bias potential from 0.00 to 4.00 V (vs. Ag/AgCl) decreases the photocurrent efficiency of nitrite ion from 40 to 34%. Therefore, applying bias potential enhances the reaction rate of nitrite ion oxidation, but the photocurrent efficiency of nitrite ion oxidation decreases gradually by increasing the applying bias potential.

3.5. Effect of light power

Increasing the light power from 360 to 640 W increases the reaction rate of nitrite ion oxidation from 6.56 to 10.48 μmol/(1 min), but the photocurrent efficiency of nitrite ion oxidation remains nearly constant, at 40%, as shown in Fig. 5. In general, a higher light power generates more holes and electrons. Both the nitrite ion oxidation rate and photocurrent value are enhanced by the generated holes and electrons. Therefore, from the definition of the photocurrent efficiency of nitrite ion oxidation, in Eq. (1), both the denominator and numerator are increases, and then the value of photocurrent efficiency of nitrite ion does not obviously change by increasing the light power.

3.6. Effect of nitrite ion concentration

Fig. 6 shows the time course of photoelectrochemical oxidation of nitrite ion in a NaCl solution. The slopes of Fig. 6 reveal that the reaction rate of the nitrite ion oxidation is maintained at a constant value, 7.60 μmol/(1 min), and is independent of the nitrite ion concentration from 0.65×10^{-4} to 4.34×10^{-4} M. The reaction rate is of zero order with respect to the nitrite ion concentration in the bulk solution. This result differs from the report in the literature [26], which stated that the nitrite ion oxidation was of first order with respect to the nitrite ion concentration by using a suspension photocatalyst.
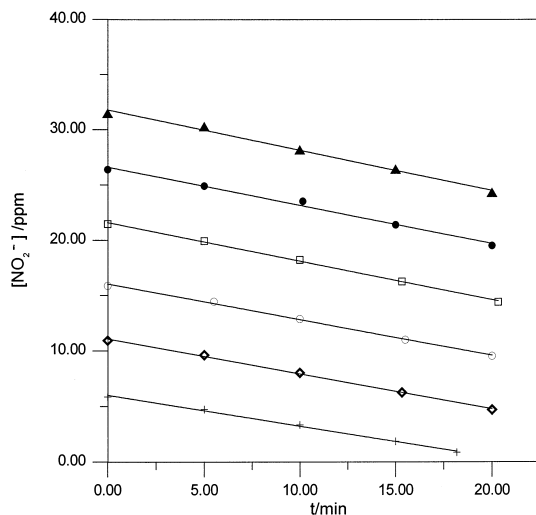

Fig. 6. Effect of nitrite ion concentration on the initial reaction rate of nitrite ion oxidation. temperature, 30°C; agitation rate, 250 rpm; potential, 2.00 vs. Ag/AgCl; electrolyte, 0.51 M NaCl, pH = 5.50; light power, 400 W.
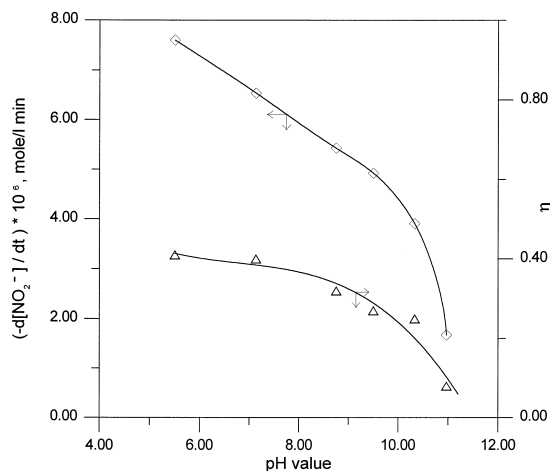
Fig. 7. Effect of pH on both the initial reaction rate and the photocurrent efficiency of nitrite ion oxidation. Initial nitrite ion concentration, 20 ppm; temperature, 30°C; potential, 2.00 vs. Ag/AgCl; agitation rate, 250 rpm; potential, 2.00 vs. Ag/AgCl; electrolyte, 0.51 M NaCl; light power, 400 W.
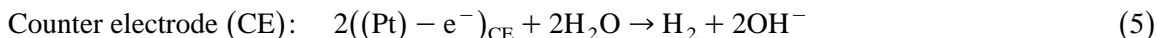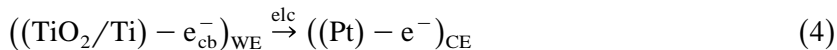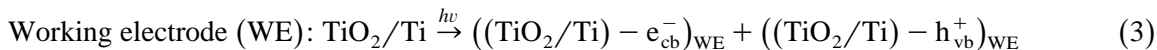
3.7. Effect of pH

Increasing the pH from 5.50 to 11.00 decreases the reaction rate from 7.60 to 1.67 μmol/(l min) as shown in Fig. 7. When the pH is larger than 10.30, the reaction rate decreases sharply. In addition, the photocurrent efficiency of nitrite ion oxidation was decreased from 40 to 8% when the pH was increased from 5.50 to 11.00, as shown in Fig. 7. Therefore, under basic conditions, both the reaction rate and photocurrent efficiency of nitrite ion oxidation decreases sharply.

4. Discussion

4.1. Photoelectrochemical mechanism on TiO_2/Ti electrode

Applying an anodic bias potential to a working electrode provides a potential gradient within the photocatalyst film to efficiently drive away the photogenerated holes and electrons at opposite directions [10,11,14,15]. From the experimental data of the photocurrent measurements, the mechanism of our device on the TiO_2/Ti working electrode and the Pt counter electrode by the applying bias potential can be expressed by Eqs. (3)–(5).

$$\text{Working electrode (WE): } TiO_2/Ti \xrightarrow{h\upsilon} ((TiO_2/Ti) - e_{cb}^-)_{WE} + ((TiO_2/Ti) - h_{vb}^+)_{WE} \tag{3}$$

$$((TiO_2/Ti) - e_{cb}^-)_{WE} \xrightarrow{elc} ((Pt) - e^-)_{CE} \tag{4}$$

$$\text{Counter electrode (CE): } 2((Pt) - e^-)_{CE} + 2H_2O \rightarrow H_2 + 2OH^- \tag{5}$$

where the subscripts cb and vb denote the conduction and valence band of the photocatalyst, respectively, and WE and CE denote the working and counter electrode, respectively.

$$\text{Total reaction: } TiO_2/Ti + H_2O \underset{h\upsilon}{\overset{elc}{\rightarrow}} 1/2H_2 + OH^- + ((TiO_2/Ti) - h^+)_{WE} \tag{6}$$
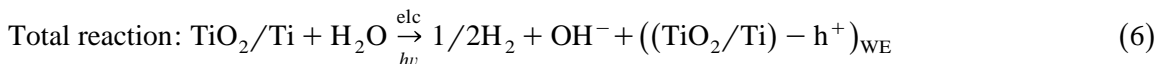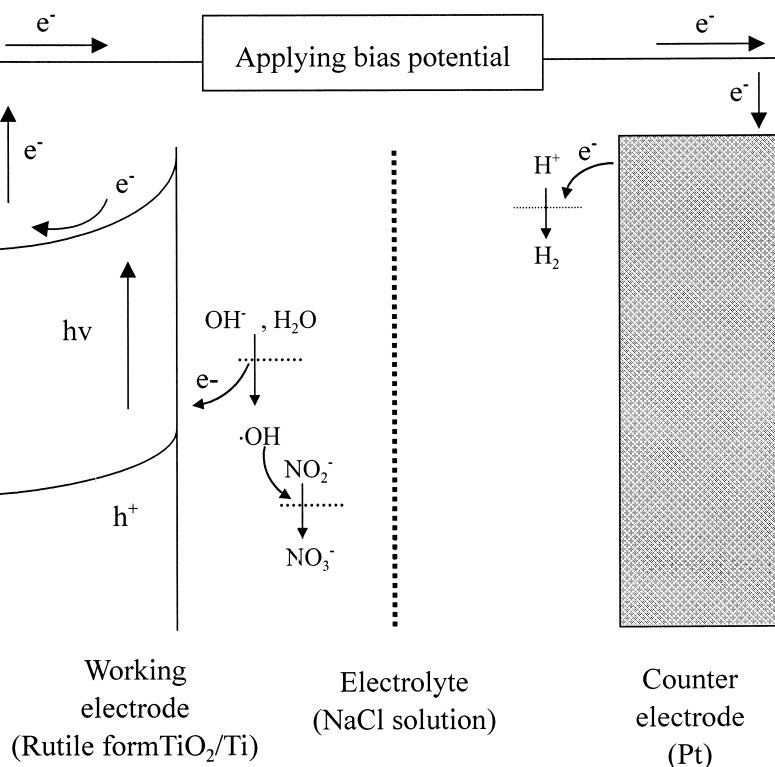
Fig. 8. Schematic illustration of photooxidation of nitrite ion and photoreduction of water by applying bias potential on the working electrode (vs. Ag/AgCl).

The schematic illustration of photooxidation of nitrite ion and photoreduction of water by applying bias potential on the working electrode are illustrated as Fig. 8. Eqs. (3) and (4) indicate that the applying bias potential makes more available holes for nitrite ion oxidation on the working electrode. Eq. (5) indicates that the photo-electrons induce the reduction reaction, and generate H_2 and OH^- on the counter electrode [35,36]. Eq. (6) is a combination of Eqs. (3)–(5), indicating that the applying bias potential promotes photoactivity of the rutile form of TiO_2 film, and makes more available holes on the electrode for the photocatalytic oxidation reaction.

In addition to the redox reactions on the working and counter electrodes, there is an important reaction on the working electrode. The reaction is the recombination of excited electrons and holes, and is the reverse reaction of Eq. (3) [37].
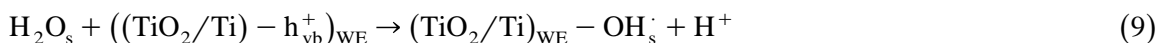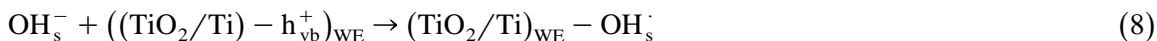
$$((TiO_2/Ti) - e_{cb}^-)_{WE} + ((TiO_2/Ti) - h_{vb}^+)_{WE} \rightarrow heat \qquad (7)$$
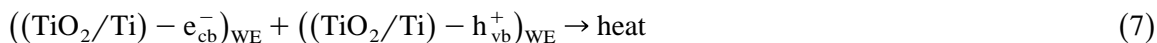
Ohko et al. [38] discussed the transfer and recombination of electrons and holes on TiO_2 film supported on a soda line glass, and indicated that the charge recombination process was a significant factor in decreasing the photocatalytic efficiency. Therefore, reducing the recombination of electrons and holes is essential to promote photocatalytic efficiency. Because Eqs. (4) and (7) are competitive reactions on the working electrode, and a higher bias potential implies a faster reaction of Eq. (4), the applying bias potential on the TiO_2/Ti electrode decreases the recombination rate of Eq. (7), and increases the photocurrent and IPCE value.

Applying high bias potential is available on this TiO_2/Ti electrode, because the excellent adhesion of the rutile form TiO_2 film can endure the high potential. Moreover, there is no dark current to

interfere with the photocurrent even at high applying bias potential. The TiO_2/Ti working electrode is a nonconductive material without irradiation. On the other hand, applying a high bias potential on TiO_2/conductive glass or TiO_2/stainless steel electrode is not permitted [39,40], because the dark current of these electrodes increases with the applying bias potential. Furthermore, the dark current at high bias potential can induce the water electrolysis on the conductive substrate of working electrode to generate oxygen [36], and the TiO_2 coated film may be destroyed.

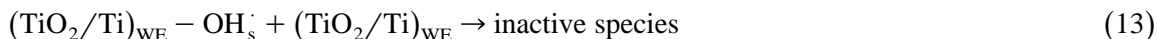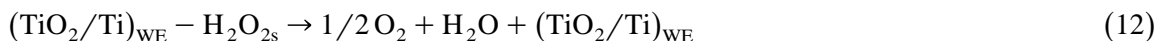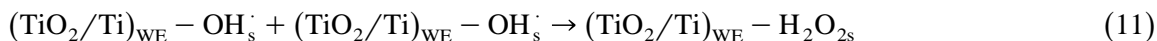### 4.2. Nitrite ion oxidation on TiO_2 / Ti electrode

The photoelectrochemical mechanism of nitrite ion oxidation on the TiO_2/Ti working electrode is proposed as follows. The holes on the TiO_2/Ti electrode react with the OH^- anion or H_2O molecules adsorbed on the TiO_2 surface, i.e., OH_s^- and H_2O_s, to generate the OH free radical [26].

$$OH_s^- + \left((TiO_2/Ti) - h_{vb}^+\right)_{WE} \rightarrow (TiO_2/Ti)_{WE} - OH_s^{\cdot} \tag{8}$$

$$H_2O_s + \left((TiO_2/Ti) - h_{vb}^+\right)_{WE} \rightarrow (TiO_2/Ti)_{WE} - OH_s^{\cdot} + H^+ \tag{9}$$

The generated OH free radical is used to oxidize the nitrite ion adsorbed on the TiO_2 surface, i.e., NO_{2s}^- [26,27]

$$2\left((TiO_2/Ti)_{WE} - OH_s^{\cdot}\right) + NO_{2s}^- \rightarrow NO_{3s}^- + (TiO_2/Ti)_{WE} - H_2O_s \tag{10}$$
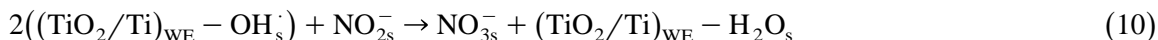
Eq. (10) is the main reaction of this photocatalytic oxidation reaction. In addition, the OH free radical on the TiO_2 surface of the TiO_2/Ti electrode may combine to generate oxygen or lose its activity at adsorbate [25,26].

$$(TiO_2/Ti)_{WE} - OH_s^{\cdot} + (TiO_2/Ti)_{WE} - OH_s^{\cdot} \rightarrow (TiO_2/Ti)_{WE} - H_2O_{2s} \tag{11}$$

$$(TiO_2/Ti)_{WE} - H_2O_{2s} \rightarrow 1/2\,O_2 + H_2O + (TiO_2/Ti)_{WE} \tag{12}$$

$$(TiO_2/Ti)_{WE} - OH_s^{\cdot} + (TiO_2/Ti)_{WE} \rightarrow \text{inactive species} \tag{13}$$

Besides the main reaction, Eqs. (11)–(13) are the side reactions of this nitrite ion oxidation.

Applying bias potential and irradiation simultaneously increases more holes on the TiO_2/Ti electrode as shown in Eq. (6), and then more OH free radicals is generated on the working electrode as shown in Eqs. (8) and (9). Therefore, the oxidation of nitrite ion is promoted as shown in Eq. (10). In addition, the more OH free radical on TiO_2/Ti electrode have the more opportunity to react each other or with the inert parts of the electrode. The OH free radicals lose its activity, which is proposed as shown in Eqs. (11)–(13). In general, increasing the pH value increase the concentration of OH free radicals in photocatalytic oxidation reaction. But the reaction rate of Eqs. (11)–(13) may be improved faster than the reaction rate of Eq. (10) on the TiO_2 film electrode at high pH. Therefore, both the percentage of OH free radicals usage and the photocurrent efficiency of nitrite ion oxidation decrease, when the pH value is increased.

Due to the electric negative charge of the nitrite ion, the applying bias anodic potential on the working electrode may increase the adsorption of nitrite ion anion. This fact results in an excess of adsorbed nitrite ion on the surface, which is one of the reasons that the reaction rate is independent of the nitrite ion in the bulk solution as shown in Fig. 6. The kinetic study of the effect of nitrite ion concentration was reported in our previous values paper [28]. When the pH is higher than pzc, i.e., the point of zero charge, negative ion, NO_2^-, are repelled on the TiO_2 surface. It has been reported that the pze of Degussa P25 TiO_2 is about pH 6.25 [1]. Therefore, considering both the adsorption of nitrite ion and the side reactions of OH free radicals on the working electrode, it can be explained that both the reaction rate and the photocurrent efficiency of nitrite ion oxidation decreases sharply under

basic conditions. In addition, the oxygen supply does not affect the reaction rate. On the other hand, supplying oxygen is an important factor in the anatase form TiO_2 photocatalyst suspension system [29], because oxygen can trap the excited electrons, and remain more holes to induce the oxidation reaction on TiO_2. The applying bias potential plays the role of trapping and transferring the excited electrons. The applying bias potential on this rutile form of TiO_2/Ti electrode is more effective than using oxygen as the electron trapper in a suspension anatase TiO_2 powder for photocatalytic oxidation reaction.

4.3. Efficiency

The efficiency of this photoelectrochemical oxidation of nitrite ion is expressed as the photocurrent efficiency of nitrite ion oxidation as shown in Eq. (1), which is similar to the definition of the current efficiency of electrochemical reaction except that the current only takes place in the presence of irradiation light. In the electrochemical reaction process, the current efficiency can be illustrated as the percentage of current for the desired reaction to the total current for all of the reactions that have occurred. Similarly, the photocurrent efficiency of nitrite ion oxidation can be expressed as the percentage of current for the nitrite ion oxidation to the total current generated by irradiation on the TiO_2/Ti electrode.

Experimental data indicates that the photocurrent efficiency of nitrite ion oxidation was about 37–40% at pH 7, as shown in Table 1. Based on the photocatalytic oxidation of nitrite ion with OH free radicals on the surface of TiO_2 [26,27] and the results of this study, 37–40% of the OH free radicals are involved in nitrite ion oxidation. Sixty to sixty-three percent of the OH free radicals carry out the side reactions on the TiO_2/Ti electrode. This fact demonstrates that the side reactions, Eqs. (11)–(13), is a significant factor in decreasing the efficiency of the photocatalytic reaction.

The photocurrent efficiency of nitrite ion decreases, when the applying bias potential increases. It can be explained that applying bias potential on TiO_2/Ti electrode promotes not only the rate of nitrite ion oxidation, but also the rate of side reactions. The latter may be higher than the former at high applying bias potential. In addition, the side reactions may increase dramatically by increasing the pH value. Therefore, the photocurrent efficiency of nitrite ion oxidation decreases sharply in a basic solution.

4.4. Comparison of the efficiency in this study with those in literature

The efficiency of the photocatalytic oxidation reaction has been extensively studied in literature [30–34,39–44]. There are several different definitions of photocatalytic or photoelectrochemical

Table 1
The photocurrent efficiency of nitrite ion oxidation with different variable

E^a (V)	$NO_2^- \times 10^4$ (M)	NaCl (M)	P^b (W)	η^c
0.5	2.17	0.51	400	0.41
1	2.17	0.51	400	0.40
2	2.17	0.51	400	0.39
2	4.34	0.51	400	0.38
2	4.34	0.34	400	0.37
2	4.34	0.34	600	0.40

[a] Applying bias potential vs. Ag/AgCl.
[b] Light power.
[c] The photocurrent efficiency of nitrite ion oxidation.

Table 2
Expression of efficiency in different photocatalytic system

Term	Expression	Reaction system	Phase	Definition	Equation	Efficiency	References
1	Quantum yield (quantum efficiency)	Film, suspension	g[a]	(number of product)/ (number of photons)	R/R_p	5–40%	[39,40]
2	Photonic efficiency	Suspension	l[b]	(reaction rate)/ (incident photon rate)	R/R_p	5–20%	[41–43]
3	Photoefficiency (PE)	Suspension	l	(reaction rate)/ (incident photon rate)	R/R_p	8–80%	[38,44]
4	IPCE	Film (TCO/TiO_2)	l	(Faraday's of photocurrent)/ (mole of incident photons)	I_p/R_p	2–80%	[30–34]
5	Light harvesting efficiency (LHE)	Film	l	(absorbed light intensity)/ (incident light intensity)	P_a/P_i	60–100%	[30]
6	Photocurrent efficiency of reactant oxidation (η)	Film (TiO_2/Ti)	l	(mole of reactant disappeared)/ (Faraday's of photocurrent)	R/I_p	8–40%	This study

[a] Gas phase reaction.
[b] Liquid phase reaction.

efficiencies. A comparison of these efficiencies in literature with our study is listed in Table 2. Quantum yield, quantum efficiency, photoefficiency and photonic efficiency are similar expression of efficiency, which are based on the number of inlet photons and amount of products formed, and are commonly used in suspension photocatalyst systems [38–44]. With these efficiencies, the reaction rate can be estimated by the measurement of inlet photons. The IPCE is also a common expression of efficiency based on the incident photons with a constant irradiation wavelength [30–34]. But the numerator of the IPCE uses photocurrent instead of reactant rate. In our study, the photocurrent efficiency of nitrite ion oxidation is based on the photocurrent measured from the working electrode and the reaction rate of nitrite ion oxidation. Moreover, on scaling up this electrochemically promoted photocatalytic process, the oxidation rate of nitrite ion can be evaluated just by the photocurrent measurement and auxiliary data, i.e., the photocurrent efficiency of nitrite ion oxidation.

5. Conclusions

The photocatalytic oxidation of nitrite ion in a NaCl aqueous solution can be electrochemically promoted by applying bias potential on the rutile form of a TiO_2 film electrode. The applying bias potential promotes the photoactivity of the rutile form of TiO_2/Ti electrode, and enhances the photocurrent density, the IPCE value and the oxidation rate of this photoelectrochemical oxidation of nitrite ion. The photoelectrochemical oxidation rate of nitrite ion is promoted by increasing both the light power and applying bias potential, and is decreased by increasing the pH, and is independence of the concentrations of nitrite ion. No oxygen supply is required to trap the excited photoelectrons in this system. The photocurrent efficiency of nitrite ion oxidation was obtained. The maximum value of the photocurrent efficiency of nitrite ion oxidation was about 40%, indicating that more than 50% of the OH free radicals lose its activity on the surface of the TiO_2 photocatalyst. The photocurrent efficiency of nitrite ion oxidation decreased slowly with increased applying bias potential, and decreased sharply with increased pH, and was almost independent of the light power. Using the value of photocurrent efficiency of nitrite ion oxidation, the oxidation rate of the nitrite ion can be evaluated by photocurrent measurement only.

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