

Adsorption Behavior and Photooxidation Kinetics of OH⁻ at TiO₂ Thin Film Electrodes*

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Abstract The adsorption behavior and photooxidation kinetics of OH⁻ at TiO₂ thin film electrodes in solution of alcohols have been studied by electrochemical measurements. The results show that the adsorption model of OH⁻ on TiO₂ surface corresponds to the Langmuir isotherm and under high enough applied bias potential the photooxidation kinetics can be described by Langmuir-Hinshelwood expression. Hydroxide ions are regarded to be the reactant with photogenerated holes and adsorbed water could not be captured by the holes and, consequently, the photocurrent is proportional to the density of OH⁻ adsorbed on TiO₂ surface under the condition of high enough light intensity. In solution with high content of alcohols, the recombining reaction between OH[·] radical and photogenerating electron can hardly occur, where the rate-limiting step is the formation of photo-driven OH[·] radical.

Keywords: Hydroxide ion, TiO₂ thin film, Photooxidation kinetic, Langmuir isotherm

There has been a growing interest in the application of TiO₂ photocatalysis towards the treatment of contaminated wastewater over the last few decades^[1-3]. Despite intensive studies of the photocatalytic reactions, there is still no clear consensus on the complete reaction kinetics. A key point of photocatalytic processes concerns the role of OH⁻. For photomineralization to proceed, the photo-generated hole must be involved in the oxidation of organic substrate either directly or *via* OH[·]. There is no substantial evidence in favor of a hole mechanism in the case of those solutes with weak affinity to solid surface such as alcohols^[4]. So, in this case the oxidation of organic compounds should depend on the kinetics of OH[·] formation.

Surely in TiO₂ suspensions, surface OH⁻ or H₂O can serve the role of traps for the photogenerated holes, forming a surface-adsorbed OH[·]^[4-6]. To our knowledge, there are no detail reports on the effect of adsorption behavior of OH⁻ on alcohols photooxidation kinetics on TiO₂ surface. In this work, we investigate the role of OH⁻ in determining photooxidation kinetics on TiO₂ thin film surface *via* photoelectrochemical techniques.

Below, we first propose the kinetics model for the photocatalytic oxidation of the adsorbed OH⁻ and indicate that the adsorption corresponds to the Langmuir isotherm. Then, the model was demonstrated through the experiments as well as by

comparison with the published literature.

Kinetics model for the photooxidation of OH⁻

When TiO₂ is immersed in water without illumination, the following reactions occur^[7].



Where subscript *s* and *soln* represent species of adsorbed and bulk solution, respectively. The bulk solution pH at which the concentration of H_s⁺ equals OH_s⁻ is called the point of zero charge (pH_{PZC}), and the pH_{PZC} of TiO₂ is reported to be pH 6.0 ± 0.2^[8]. Fig. 1 represents schematically variation on TiO₂ surface at different pHs. To simplify, we assume that the Ti atom sites can be divided into two kinds at pH_{PZC}. One kind is sites adsorbed with OH⁻, the other being ones adsorbed with associated H₂O molecules, as shown in Fig. 1(a). When solution pH lowers from pH_{PZC}, reaction I proceeds in right direction, which results in a decrease of adsorbed OH⁻ on TiO₂ surface, as shown in Fig. 1(b). Similarly, When solution pH increases from pH_{PZC}, reaction II proceeds in right direction, and in the meanwhile the associated H₂O molecules are partly replaced by solution OH⁻ ions to form adsorbed OH⁻, which leads to a net increase of adsorbed OH⁻ on TiO₂ surface, as shown in Fig. 1(c).

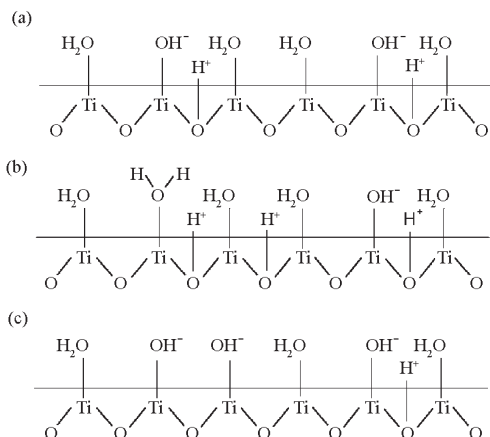


Fig. 1 Schematic diagram of the adsorbed species on TiO₂ surface in solution with pH lower than PZC (a), at PZC (b) and higher than PZC (c)

Now let us consider the net transfer of charge across the interface. Anodic and cathodic electrical current related to charge transfer would be denoted as I_a^H and I_c^H , respectively. On illumination, net current I_{net} can be written as:

$$I_{net} = I^H = I_a^H - I_c^H \quad (1)$$

Neglecting the dark current when the interfacial charge transfer is the rate-determining step, the photocurrent is determined by the rate of interfacial charge transfer. So, the photocurrent I_{ph} can be written as:

$$I_{ph} = I_a^H - I_c^H = nFk_1 [h^+]_{surf} C_{Red} - nFk_2 C_{Ox} \quad (2)$$

Where subscript surf represents adsorbed species, C_{Ox} and C_{Red} represent the concentrations of oxidizing and reducing agent at the semiconductor/electrolyte interface, respectively. k_1 and k_2 are the rate constants of oxidation and reduction reaction, respectively. n is electron transfer number; F is Faraday constant.

At open circuit, the photocurrent is zero. Under high enough anodic polarized, firstly, let us consider the cathodic reaction. The photogenerated electrons at the semiconductor surface are rare as they are withdrawn by the applied potential, meanwhile purging with nitrogen in solution, the cathodic reaction can hardly occur, thus I_c^H can be neglected, we get:

$$I_{ph} = I_a^H - I_c^H = nFk_1 [h^+]_{surf} C_{Red} \quad (3)$$

Secondly, about the anodic reaction, we assume that only adsorbed OH⁻ can be oxidized by photogenerated holes while the adsorbed H₂O molecules do not. This is believable at least in point of thermodynamics ($H^+ + OH^- + e \rightarrow H_2O$, $\Phi^0 = 2.85$ V (vs NHE); $OH^- + e \rightarrow OH^{\cdot}$, $\Phi^0 = 2.02$ V (vs NHE); Φ_{vb}^0 (TiO₂) = 2.7 V (vs NHE)). This means the anodic reaction is exclusive as follows:



So, based on above consideration, we have:

$$I_{ph} = I_a^H = nFk_1 [h^+]_{surf} C_{OH_s^-} \quad (4)$$

Where $C_{OH_s^-}$ is the concentration of the adsorbed OH⁻.

Additionally, we have to give some consideration as to the further surface electrochemical process. With efficient enough scavengers of OH[·], (e.g. methanol^[9]), the recombination reaction of OH[·] with electrons, which decreases the photocurrent, can be repressed. Even if OH[·] is not consumed totally, the photocurrent may be revised by introducing a coefficient P_{or} . Meanwhile, the intermediate products may inject electron to the semiconductor, thus the photocurrent also needs to be revised by introducing a doubling factor of photocurrent γ . So, in this case the photocurrent can then be expressed as:

$$I_{ph} = P_{or} \gamma nFk_1 [h^+]_{surf} C_{OH_s^-} \quad (5)$$

Where P_{or} denotes the encounter probability of OH[·] with alcohol molecular; γ represents the doubling factor of the photocurrent of alcohol oxidation.

The surface concentration of photogenerated holes $[h^+]_{surf}$ should be proportional to the incident light intensity. Under high enough light intensity, $[h^+]_{surf} \approx \text{constant}$, thus the photocurrent is predominantly determined by the concentration of adsorbed OH⁻. So, under a constant high light intensity, from equation (5) we obtain:

$$I_{ph} = P_{or} \gamma nFk_1 [h^+]_{surf} C_{OH_s^-} = k C_{OH_s^-} \quad (6)$$

Where, $k = P_{or} \gamma nFk_1 [h^+]_{surf}$ is a constant.

In the domain of pH \geq pH_{PZC}, both the original adsorbed OH⁻ and the increasing part of OH⁻ resulting from the substitution of the adsorbed H₂O molecules by OH⁻, are contributed to the total photocurrent I_{ph}^{total} . Based on equation(6), the increasing part of photocurrent is:

$$I_{ph}^{incr} = I_{ph}^{total} - I_{ph}^{PZC} = k C_{OH_s^-}^{incr} \quad (7)$$

Where I_{ph}^{PZC} is the photocurrent resulting from the original adsorbed OH⁻ at pH_{PZC}.

We further recognize that OH⁻ may adsorb on the TiO₂ surface prior to electron transfer. Otherwise, the photocurrent will be independent of the solution pH, which is not observed in the experiments. Here, we presume that the adsorption behavior of OH⁻ on TiO₂ surface fits Langmuir sorption model. So, we have:

$$C_{OH_s^-} = C_{OH_s^-}^{max} \frac{K_{OH^-} [OH^-]_b}{1 + K_{OH^-} [OH^-]_b} \quad (8)$$

Where $C_{OH_s^-}$ represents the concentration of OH⁻ sorbed to the surface; $C_{OH_s^-}^{max}$ is the saturate absorption concentration. K_{OH^-} represents the equilibrium constant for sorption of OH⁻. $[OH^-]_b$ represents the OH⁻ concentration in bulk solution.

Substituting eq. (8) into eq. (7), rearranging, we get:

$$\frac{1}{I_{ph}^{incr}} = \frac{1}{k' K_{OH^-}} \frac{1}{[OH^-]_b} + \frac{1}{k'} \quad (9)$$

With efficient enough scavengers of OH[•], under high enough applied bias potential the photocurrent is saturated. So, equation (9) can then be rewritten as:

$$\frac{1}{I_{\text{phs}}^{\text{inc}}} = \frac{1}{k' K_{\text{OH}^-}} \frac{1}{[\text{OH}^-]_{\text{b}}} + \frac{1}{k'} \quad (10)$$

Where $I_{\text{phs}}^{\text{inc}}$ represents the saturated photocurrent

This suggests that when it was plotted by $(I_{\text{phs}}^{\text{inc}})^{-1}$ vs $([\text{OH}^-]_{\text{b}})^{-1}$ from equation (10), a straight line should be obtained, and K_{OH^-} and k' can be calculated through the slope and intercept.

1 Experimental section

1.1 Chemicals

Titanium butoxide (97%), methanol (99.8%) and sodium sulphate (99.7%) were obtained from Shanghai Third Chemical Reagent Co. of China. Other chemicals were of reagent grade and used without further purification. Deionised water ($\rho = 18 \text{ M}\Omega \cdot \text{cm}$) was used for all rinsing and aqueous solutions.

1.2 Preparation of TiO₂ film electrode

The TiO₂ thin film was prepared by the sol-gel technique described in Ref. [10]. Exposed area of the TiO₂ film was 0.5 cm², the rest was covered with epoxy resin.

1.3 Apparatus and methods

Electrochemical measurements were carried out in a standard three-electrode system at 25 °C. The TiO₂ film was used as working electrode, a saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes, respectively. A Potentiostat/Galvanostat Model 273 (Princeton Applied Research) was used in photoelectrochemical measurements. The incident light emitted from a 250 W xenon lamp (Type SVX 1450, Müller Elektronik Optik, Germany) was focused on the electrode surface from the electrolyte side. The incident light intensity uncorrected in the solution was 15.3 mW · cm⁻² calibrated by optometer S370 (UDT instruments,

U. S. A). The solution pH was adjusted by sulphuric acid or sodium hydroxide. All experiments were conducted under N₂ atmosphere unless specified.

2 Results and discussion

2.1 Influence of OH⁻ on the photocurrent in blank solutions

Fig. 2 shows the linear sweep voltammetry recorded at TiO₂ thin film electrodes under illumination in blank electrolyte at three pH values. As shown in the figure, the saturated photocurrents I_{phs} grow with pH, while the E_{on} (the onset potential of photocurrent) is shifted more negative as pH increases.

Hydronium and hydroxide ions that can change the surface potential of TiO₂ are so-called potential-determining ions^[11-12]. Addition, Nakato *et al.* [13] have argued that the Ti-OH groups on TiO₂ surface can not be oxidized totally by photogenerated holes. This may be available for particulate TiO₂ electrodes. In other words, there should be a certain relationship between saturated photocurrent and the concentration of the adsorbed OH⁻ on TiO₂ surface.

2.2 Influence of OH⁻ on the photocurrent in solutions with methanol

Fig. 3 shows the dependence of I_{phs} on methanol concentrations at three pH values. The methanol concentration corresponding to that I_{phs} began saturated is in a rather close proximity, with methanol $\sim 0.2 \text{ mol} \cdot \text{L}^{-1}$.

Fig. 4(a) shows a series of linear sweep voltammetry results recorded under illumination at different pH values with 0.6 mol · L⁻¹ methanol. The saturated photocurrent I_{phs} in associated with photooxidation of 0.6 mol · L⁻¹ solution of methanol was found to be much larger than that corresponding to the photooxidation of water, as shown from Fig. 2. Such a behavior is indicative of the resistance of the photogenerated OH[•] and electron recombination. In blank solution, due to absence of OH[•] scavenger, the recombination reaction could occur quickly

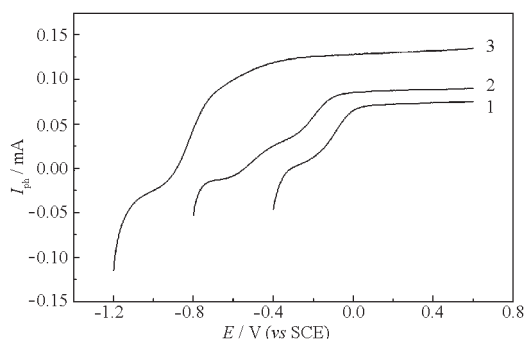


Fig. 2 Linear sweep voltammetry of electrode in blank solutions of different pH values under illumination (15.3 mW · cm⁻²) pH: (1)1.32, (2)6.99, (3)12.97

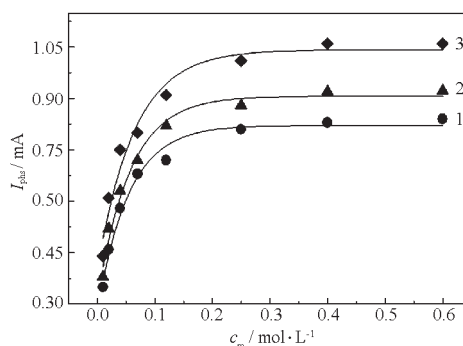


Fig. 3 The dependence of the saturated photocurrent on methanol concentration at different pH values pH: (1)1.32, (2)6.98, (3)12.97

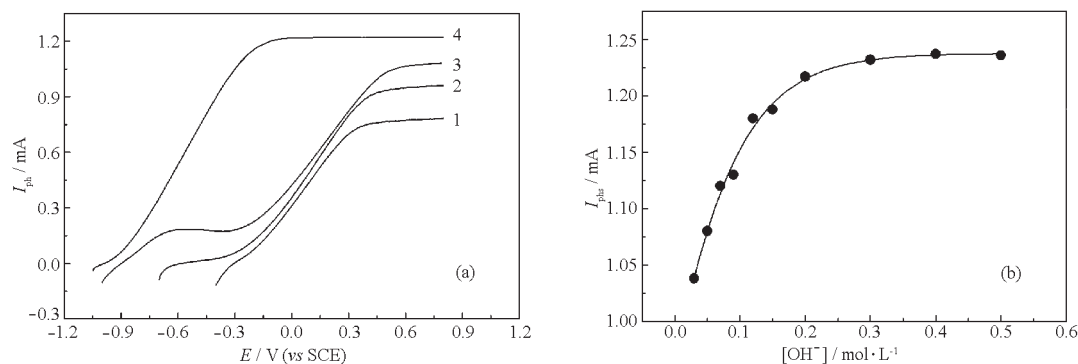


Fig. 4 (a) Linear sweep voltammetry of electrode in methanol solutions ($0.6 \text{ mol} \cdot \text{L}^{-1}$) of different pH values under illumination ($15.3 \text{ mW} \cdot \text{cm}^{-2}$)
(b) The dependence of the saturated photocurrent with $0.6 \text{ mol} \cdot \text{L}^{-1}$ methanol on hydroxide ion concentration

pH: (1) 1.32, (2) 8.99, (3) 12.97, (4) 13.51

and particularly, the extent of recombination is different at various pH values, thus decreasing the photocurrent. With high enough and efficient scavengers methanol, the recombination reaction can be largely repressed. To keep the same extent of recombination in different pH solutions, we set $0.6 \text{ mol} \cdot \text{L}^{-1}$ methanol in solution so as to obtain a relationship between I_{phs} and the concentration of adsorbed OH^- species on the electrode surface.

Fig. 4(b) shows particularly the partial dependence of the saturated photocurrent on OH^- concentration corresponding to pH from 12.48 to 13.70 in $0.6 \text{ mol} \cdot \text{L}^{-1}$ methanol solutions. Based on the results of Fig. 4(b), the plot of the reciprocal rate ($I_{\text{phs}}^{\text{sat}})^{-1}$ (pH_{PZC} is 6.0) as a function of the reciprocal ($[\text{OH}^-]_{\text{b}})^{-1}$ yields a straight line, as indicated in Fig. 5. The linear transform of this expression yields $K_{\text{OH}^-} = 16.53$ (with linear coefficient $R^2 = 0.9964$) for the case of methanol oxidation. Similarly, We obtained $K_{\text{OH}^-} = 17.44$ for ethanol ($R^2 = 0.9977$) and $K_{\text{OH}^-} = 14.91$ for tert-butanol ($R^2 = 0.9980$), respectively. The average value of them is $K_{\text{OH}^-} = 16.29$. This fits well to equation (10). This means that the proposed kinetics model is believable, or the photocatalytic oxidation of OH^- corresponds to L-H (Langmuir-Hinshelwood) model.

2.3 Independent experiment evidence

To further confirm this model, an experiment was conducted to measure K_{OH^-} for sorption of OH^- on TiO_2 surface. One gram of TiO_2 powder was added in a vessel with six milliliters $0.6 \text{ mol} \cdot \text{L}^{-1}$ methanol aqueous solution of a certain pH in the range of from pH 12.00 to pH 13.60, and stirred fully. The pH of the supernatant was measured, thus the quantity of the adsorbed OH^- ions can be obtained by the pH difference before and after adsorption. It is found that K_{OH^-} of OH^- on TiO_2 powder is 18.09, coincident with the one obtained

from Fig. 5.

2.4 Comparison with result in literature

As reported by Ref. [4], the charge transfers occurring at the TiO_2 semiconductor/electrolyte can be depicted by a set of reactions. Under high enough bias potential and concentration of alcohols, recombination reaction hardly occurs, the reaction rate (denoted as saturated photocurrent) can be expressed as following:

$$I_{\text{phs}} = nFk_2 [h^+] [\text{OH}_s^-] \quad (11)$$

Equation (11) and (4) is almost identical, which supports the derived model.

2.5 Further notes on the kinetics model and implications to photocatalysis

It is necessary to point out that it does not fit L-H model when the concentration of OH^- is beyond the range of 0.01 to $0.5 \text{ mol} \cdot \text{L}^{-1}$. It may be explained as following: (a) the adsorption of OH^- on TiO_2 surface deviates Langmuir sorption isotherm at too low or too high concentration; (b) the sorption

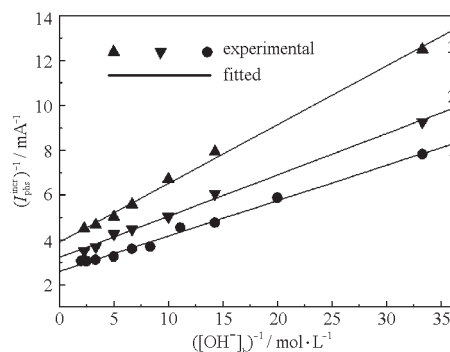


Fig. 5 The plot of reciprocal saturated photocurrent vs the reciprocal concentration of OH^- with alcohols (1) $0.6 \text{ mol} \cdot \text{L}^{-1}$ methanol; (2) $0.6 \text{ mol} \cdot \text{L}^{-1}$ ethanol; (3) $0.6 \text{ mol} \cdot \text{L}^{-1}$ tert-butanol

rate of OH⁻ is not so rapid as that of consumption, particularly at low pH.

3 Conclusions

It has demonstrated that the adsorption model of OH⁻ on TiO₂ surface corresponds to the Langmuir isotherm and under high enough applied bias potential the photooxidation kinetics can be described by Langmuir-Hinshelwood expression. OH⁻ is regarded to be the main reactant with photogenerated holes in aqueous solution of alcohols; consequently, the photocurrent is proportional to the coverage of OH⁻ adsorbed on TiO₂ surface. In solution with high content of alcohols, the recombining reaction between OH[·] radical and photogenerated electron can hardly occur, where the rate-limiting step is the formation of photo-driven OH[·] radical. So, under a certain light intensity the degradation rates of alcohols at starting time should mainly dependent on their encounter frequencies with OH[·]. Anyway, this insight should provide a better understanding of the role of OH⁻ in the photoelectrocatalytic kinetics.

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氢氧根离子在 TiO₂ 薄膜电极上的吸附行为和光氧化动力学*

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摘要 在醇的水溶液中, 应用电化学方法研究了 OH⁻ 在 TiO₂ 薄膜电极上的吸附行为和光氧化动力学. 实验结果表明, OH⁻ 在 TiO₂ 表面的吸附模型符合 Langmuir 等温吸附方程式, 其光氧化动力学行为能用 Langmuir-Hinshelwood 动力学方程来描述. 在光强足够大时, 光电流和 OH⁻ 在 TiO₂ 表面的吸附浓度成正比, 这表明, 光生空穴仅氧化吸附于 TiO₂ 表面的 OH⁻, 同时吸附的水分子则不能被氧化. 在醇浓度足够高的溶液中, 自由基 OH[·] 和电子之间的复合反应几乎不发生, 这时整个光氧化反应的速控步骤是光生自由基 OH[·] 的生成.

关键词: OH⁻ 离子, TiO₂ 薄膜, 光氧化动力学, Langmuir 等温吸附方程式

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