

Effect of Chemical Treatment on TiO₂ Particles by IMPS

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The photodegradation reaction rate of CHCl₃ in TiO₂ particulate suspension was improved significantly by HCl-treatment. The effect of HCl-treatment on the photocatalytic activity of TiO₂ was studied in a PEC cell by using Intensity-Modulated Photocurrent Spectroscopy (IMPS). The magnitude of photocurrent response and the characteristic frequencies of the upper and lower semicircles in the complex plane of IMPS response were analyzed, and the cathodic and anodic reaction processes of photogenerated holes and electrons were discussed. The increases in the cathodic and anodic photocurrent response and in the time constants of both cathodic and anodic reaction processes indicate that HCl-treatment leads to the improvement of the photocatalytic activity of TiO₂ and a change of the photocatalytic kinetic mechanism.

Keywords photodegradation, TiO₂ particulate suspension, photocatalytic activity, HCl-treatment, IMPS

Introduction

Photocatalysis of semiconductor particulate system provides a cheap and convenient method for the degradation of a wide range of harmful chemicals for environmental protection applications.^{1,2} TiO₂, which is chemically inert, has been widely used as effective photocatalyst in a particulate suspension system.³ Recently, much attention has been paid to search the feasible ways for improving the photocatalytic activity of TiO₂, such as expanding the wavelength response for increasing the quantum efficiency in the visible region by transition metal doping^{4,5} and altering surface characteristics namely surface area, surface crystallinity, surface charge, *etc.*, by optimization of the

preparation.⁶ Our previous work indicated that chemical treatment strongly influenced the surface characteristics of TiO₂ particles⁷⁻⁹ and improved the photocatalytic activity remarkably.¹⁰ In this work, we report a mechanical study of the effect of chemical treatments on improving the photocatalytic activity of TiO₂ particles by using Intensity-Modulated Photocurrent Spectroscopy (IMPS).

IMPS known as the optical nonstationary technique has been used to investigate the kinetic processes at semiconductor/electrolyte interface.¹¹ By measuring the photocurrent response of modulated excitation intensity, the kinetics of photocharge transfer, surface recombination including surface states relaxation processes can be analyzed over several decades of frequency (10⁻³—10⁶ Hz).¹²⁻¹⁵ Generally, the photocurrent response of photogenerated holes and electrons have opposite signs and will not be in phase. The interfacial kinetic processes of photogenerated holes and electrons can be therefore studied separately. Photocatalysis of TiO₂ particles is initiated by the charge transfer of photogenerated holes and electrons to the pollutant species resulting in the redox reactions at TiO₂ particles/solution interface. The kinetic processes of photogenerated holes and electrons transfer at TiO₂ particles interface analogous to that at semiconductor electrode interface can be studied by IMPS measurements in a TiO₂ particulate suspension PEC cell.¹⁶

Experimental

TiO₂ powder (99.9%, anatase) was purchased from

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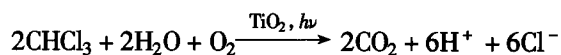
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Beijing Fine Chemicals Co. Ltd. and used as received. Chemical treatment was performed by dipping the TiO₂ powder in HCl solution 6 mol/L for 16 h followed by fully washing and drying up. TiO₂ particulate suspensions were prepared by ultrasonic dispersion of TiO₂ powders before and after HCl-treatments in triply distilled water at a concentration 0.1 g/L containing KCl (0.1 mol/L). Photodegradation experiments were carried out in the TiO₂ particulate suspension (pH = 5) containing chloroform (3 × 10⁻³ mol/L), using 29 W low pressure Hg lamp as the light source. A chloride selective electrode was used to determine the production of Cl⁻ during photodegradation of chloroform. The remained chloride on HCl treated TiO₂ particles checked in a control experiment was negligible. Collecting photocurrent from the irradiated TiO₂ particulate suspension was achieved in a conventional three-electrode PEC cell with a quartz window. Two 4-cm² Pt foils were used as working and counter electrodes. The working electrode was placed in the cell parallel and closed to the quartz window and the counter electrode was placed at the position vertical to the working electrode and kept it out of irradiation. A saturated calomel electrode (SCE) was used as reference electrode. TiO₂ particulate suspension PEC cell was deaerated by ultrapure N₂ before and during the measurements. Light source was 125 W high-pressure Hg lamp. In the IMPS measurements, the incident light was modulated by adding a sinusoidal voltage generated by a PAR 5301 lock-in amplifier to the lamp power supply. The modulated photocurrents response was measured in the frequency range of 5 Hz—1 kHz via PAR 273 potentiostat/galvanostat and lock-in amplifier. The sinusoidal modulation level of the light intensity was < 5%. The total phase shifts and the attenuation of amplitude of the photocurrent amplitude were checked with respect to the reference signal using a Si solar cell and made correction for the phase and amplitude of the photocurrent.¹⁸ All the experiments were performed at the room temperature.

Results and discussion

Photocatalytic degradation of chloroform on TiO₂ occurs according to the following stoichiometry:^{1,19}



the photodegradation rate of chloroform can be determined

by measuring the concentration of produced chloride [Cl⁻] as a function of irradiation times. Fig. 1 shows the production rate of chloride for the photocatalytic degradation of CHCl₃ (3 × 10⁻³ mol/L) in TiO₂ particulate suspension under air. The photocatalytic activity of TiO₂ particulate before and after HCl-treatment on the degradation of CHCl₃ was compared in this figure. It can be seen in both cases that [Cl⁻] increased linearly during the initial irradiation time of 60 min and then the production rate of chloride decreased. A larger production rate of chloride obtained in the HCl-treated TiO₂ particulate suspension indicates that the photocatalytic activity of TiO₂ particles is increased by HCl-treatment.

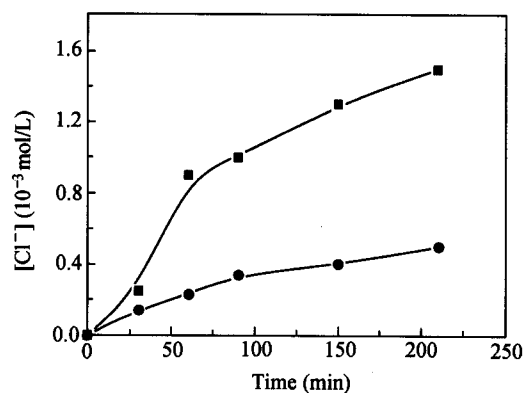


Fig. 1 Photodegradation of 3 × 10⁻³ mol/L CHCl₃ in 1 g/L TiO₂ particulate suspension ●: before HCl-treatment, ■: after HCl-treatment.

In order to examine the effect of HCl-treatment on the photocatalytic activity of TiO₂ particles, the kinetic processes of photogenerated holes and electrons occurring at TiO₂ interface were analyzed from the IMPS response measured in a particulate suspension PEC cell in the absence of redox species. In the irradiated TiO₂ particulate suspension PEC cell, photogenerations of holes and electrons occur at particle surface. Photogenerated hole forms rapidly a hydroxylate radical (OH[•]) which reacts in the following reaction to produce H₂O₂. Photogenerated electron traps in the TiO₂ particles (TiO₂⁻), and oxidizes subsequently at the Pt working electrode generating an anodic photocurrent. Reduction of hydroxyl radical (OH[•]) can also occur at Pt working electrode leading to produce a cathodic photocurrent. Therefore, collecting the photogenerated charges as the photocurrent response from the irradiated TiO₂ particulate suspension is feasible.

Fig. 2 shows the photocurrent response collected from the irradiated TiO_2 particulate suspension ($\text{pH} = 5$) under the applied potential of 0.6 V vs. SCE. An anodic photocurrent appeared and rose sharply to attain a steady state level when light was turned on. This anodic photocurrent decayed to zero when light was turned off. In a control experiment under the identical conditions except for the absence of TiO_2 particulate suspension, the photocurrent response disappeared. This demonstrates that the observed photocurrent response shown in Fig. 2 was produced from the irradiated TiO_2 particulate suspension.

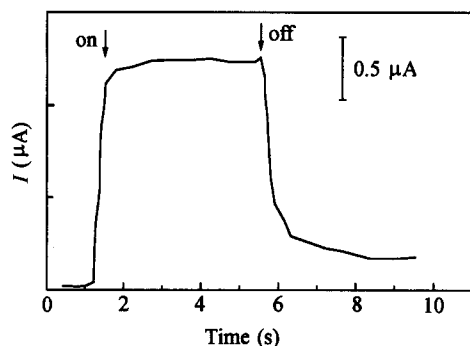


Fig. 2 Collecting photocurrent-time response in 0.1 g/L TiO_2 particulate suspension containing 0.1 mol/L KCl, applied potential 0.6 V vs. SCE.

Actually, the steady anodic photocurrent collected from the TiO_2 particulate suspension is a composite of both the anodic and cathodic photocurrents that can be known from the IMPS measurements. Fig. 3 is the complex plane

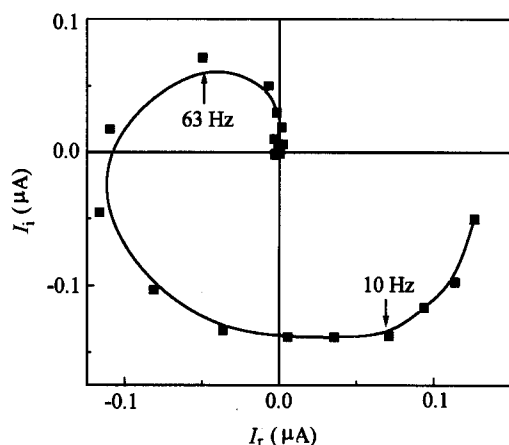
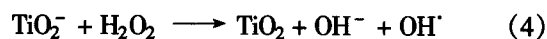
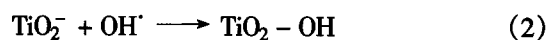
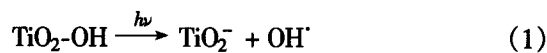


Fig. 3 Complex plane of IMPS response in 0.1 g/L TiO_2 particulate suspension containing 0.1 mol/L KCl, applied potential 0.6 V vs. SCE.

plot of IMPS response which was obtained by collecting the frequency dependent photocurrent response from the TiO_2 particulate suspension PEC cell under intensity-modulated light irradiation and an applied potential of 0.6 V vs. SCE. It can be seen that the complex plane of the IMPS response is composed of an upper semicircle locating at the second quadrant of higher frequency region and a lower semicircle locating at third and fourth quadrants of lower frequency region. From the fact that the complex plane of IMPS response can not be detected in the irradiated PEC cell without TiO_2 particulate suspension, we suggest that the complex plane of IMPS response results in the cathodic and anodic reactions of photogenerated holes and electrons of TiO_2 particles. The mechanism of photocatalytic processes of TiO_2 particles is suggested as the following equations:¹⁹



where $\text{TiO}_2\text{-OH}$ represents TiO_2 particle with surface hydroxylated group, TiO_2^- and OH^{\cdot} represent the photogenerated electrons and holes trapped on the TiO_2 particle and hydroxylate, respectively. Eq. (1) is the reaction of charge separation under band gap irradiation; Eq. (2) represents the direct recombination reaction; Eqs. (3) and (4) are the reactions of indirect recombination; Eqs. (5) and (6) are the reduction and oxidation reactions of photogenerated radicals OH^{\cdot} and TiO_2^- at Pt working electrode to generate the cathodic and anodic photocurrents, respectively. Based on the proposed mechanism, the upper and lower semicircles in the complex plane of IMPS response are assigned to the cathodic reduction and anodic oxidation reactions of photogenerated radicals OH^{\cdot} and TiO_2^- , *i. e.*, the reactions of Eqs. (5) and (6), respectively.

Fitting the IMPS response plot with the frequency domain dual exponential decay formula, the cathodic and anodic reactions of photogenerated radicals OH^\cdot and TiO_2^- can be analyzed in terms of the parameters: the magnitude of the cathodic and anodic photocurrents and the time constants of cathodic and anodic reactions which are defined as the inverse of the characteristic frequencies of both reactions.

$$I(f) = A_a \frac{1 + j \cdot f/f_a}{1 + f^2/f_a^2} - A_c \frac{1 + j \cdot f/f_c}{1 + f^2/f_c^2} \quad (7)$$

where $I(f)$ is the frequency dependent photocurrent, A_a and A_c are the magnitude of the anodic and cathodic photocurrents, f_a and f_c are the characteristic frequencies of the anodic and cathodic reactions respectively. The fitting results are listed in Table 1. As shown in Table 1, the cathodic photocurrent is much smaller than the anodic photocurrent. This is arisen from a decrease of the concentration of OH^\cdot due to the consumption of OH^\cdot in the Eq. (3). As the result of a smaller cathodic photocurrent compared to the anodic photocurrent, the collected photocurrent as the composite of the anodic and cathodic photocurrents shows in Fig. 2 is anodic. The time constant of cathodic reaction ($1/f_c$) is smaller than that of anodic reaction ($1/f_a$) indicating that the cathodic reaction is a faster process and the anodic reaction is a slower process.

Fig. 4 shows the complex plane plot of IMPS response measured from the irradiated TiO_2 particulate suspension after HCl-treatment. The fitting parameters are also given in Table 1. It can be seen that both the anodic and cathodic photocurrents obtained from the TiO_2 particulate suspension after HCl-treatment are significantly larger than that of TiO_2 particulate suspension without HCl-treatment. Moreover, a larger cathodic photocurrent than the anodic photocurrent is observed. The increases of the cathodic and anodic photocurrents indicate that the photocatalytic activity of TiO_2 particulate suspension is improved after HCl-treatment. There are two effects of the HCl-treatment on the surface of TiO_2 particles leading to improve their photocatalytic activity are considered: (1) HCl-treatment can passivate the surface states which behave as surface recombination centers of TiO_2 particles. In this case, the photocharge recombination reaction [Eq. (2)] is reasonably suppressed. An increase of the photo-generated holes and electrons taking part in the cathodic and anodic reactions (Eqs. 5 and 6) at the Pt working

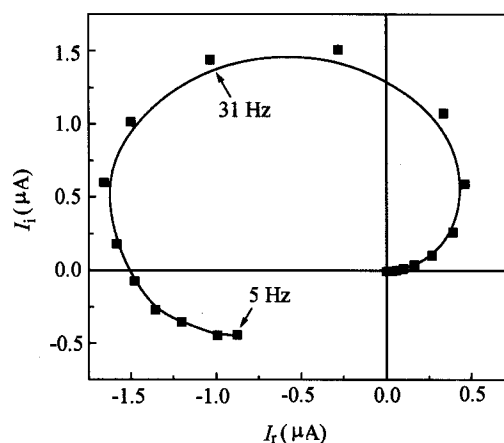


Fig. 4 Complex plane of IMPS response in the 0.1 g/L TiO_2 particulate suspension after HCl-treatment, containing 0.1 mol/L KCl, applied potential 0.6 V vs SCE.

electrode results in the generation of larger cathodic and anodic photocurrents, respectively. (2) The surface hydroxylated groups of TiO_2 (anatase) show an acidic character,²⁰ HCl-treatment may change the density of surface hydroxylated groups,²¹ *i. e.*, the surface acidity of TiO_2 particles, which can be examined by FTIR spectroscopy measurements. An increase in the intensity of the vibrational mode of surface hydroxylated group [$\text{OTi}(\text{OH})_2$] at 1089.4 cm^{-1} is pointed out in the FTIR spectrum of HCl treated TiO_2 particles indicating the surface acidity of TiO_2 particles is increased.²² The oxidation of H_2O_2 with TiO_2^- [Eq. (4)] will be favored by an increase of the surface acidity of TiO_2 particles giving rise to generate more OH^\cdot and consume partial TiO_2^- in this reaction. This leads to generate a larger cathodic photocurrent in the cathodic reaction [Eq. (5)] compared to the anodic photocurrent generating in the anodic reaction [Eq. (6)].

As shown in the Table 1, the time constants of the cathodic and anodic reactions after HCl-treatment are both increased compared to that of respective reactions without HCl-treatment. This implies that the cathodic and anodic reaction rates are decreased. Presumably, the decreases in the cathodic and anodic reaction rates are obtained from the strong influence of HCl-treatment on the reaction of Eq. (4). These results indicate a change of photocatalytic kinetic mechanism occurred in the irradiated TiO_2 particulate suspension after HCl-treatment. Further analysis of the photocatalytic mechanism of HCl treated

Table 1 Cathodic and anodic photocurrents and the characteristic frequencies of cathodic and anodic reactions obtained by curves fitting from Figs. 3 and 4

Applied potential (V vs. SEC)	A_c (μA) ^a		A_a (μA) ^a		f_c (Hz) ^b		f_a (Hz) ^b	
	HCl-treatment							
	before	after	before	after	before	after	before	after
0.4	0.13	0.62	0.27	0.57	68	38	15	6
0.6	0.15	1.70	0.32	1.50	65	36	13	5

^a A_c and A_a are the magnitudes of the cathodic and anodic photocurrents. ^b f_c and f_a are the characteristic frequencies of the cathodic and anodic reactions.

TiO₂ particulate suspension by the aids of digital simulation is in the progress.

Conclusion

IMPS was used to study the photocatalytic mechanism of TiO₂ in a particulate suspension PEC cell. A complex plane of IMPS response is composed of the upper and lower semicircles represent the reduction and oxidization processes of the photogenerated OH⁻ and TiO₂⁻, *i.e.*, the cathodic and anodic reactions, respectively. The photocatalytic mechanism and the improvement of the photocatalytic activity of TiO₂ particulate suspension by HCl-treatment was analyzed by determining the magnitude of the cathodic and anodic photocurrents and the characteristic frequencies of the cathodic and anodic reactions. The increases of cathodic and anodic photocurrents are attributed to the passivation of the surface states and the increase of the surface acidity of the TiO₂ particles. A change of the photocatalytic kinetic mechanism is suggested for the TiO₂ particulate suspension after HCl-treatment in terms of the increased time constants of both cathodic and anodic reactions.

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