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Photoelectrochemical measurement of phthalic acid adsorption on porous TiO_2 film electrodes

Dianlu Jiang[a], Huijun Zhao[a,*], Shanqing Zhang[a], Richard John[a], Geoffrey D. Will[b]

[a] School of Environmental and Applied Sciences, Griffith University, Gold Coast Campus, PMB 50, Gold Coast Mail Center, QLD 9726, Australia
[b] Center for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

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Abstract

A new adsorption measurement method based on photoelectrochemical oxidation principles has been developed. The method can be used to directly quantify the amount of adsorbates at a TiO_2 electrode surface in a sensitive and accurate manner. The adsorption of phthalic acid was studied as a test case. The relationship between the amount of adsorbate at the TiO_2 surface and the concentration of phthalic acid in the solution was obtained. The adsorption of phthalic acid on TiO_2 surface was shown to follow a Langmuir type adsorption model. For the first time, the adsorption equilibrium constant of an adsorbate at TiO_2 surface has been photoelectrochemically measured. The adsorption equilibrium constant of phthalate on TiO_2 porous film at pH 4.0, $K = 4.0 \times 10^4\,M^{-1}$, was obtained using our method, which was close to that obtained by conventional methods. The effect of solution pH on the amount of adsorbate at TiO_2 surface was also investigated. The results indicate the adsorption of phthalic acid is mainly of chemical bonding nature.

Keywords: Nanoporous TiO_2 film; Adsorption; Photoelectrochemistry; Phthalic acid

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1. Introduction

In recent years, photocatalytic processes at the semiconductor, TiO_2, have been used to great effect in the oxidative degradation of organic compounds in solution [1–7]. The theoretical basis of TiO_2 photocatalysis is well established and involves light induced photogeneration of electron–hole pairs within the semiconductor catalyst [3,6,8]. These electron–hole pairs dissociate into free photoelectrons in the conduction band (e_{cb}^-) and photoholes in the valence band (h_{vb}^+). The photohole formed at TiO_2 is a very powerful oxidising agent ($E^0 = +3.1\,V$ versus NHE) that will readily lead to the oxidation of an adsorbed species at the TiO_2–liquid interface. In this way, direct oxidation of adsorbed organic material and/or solvent molecules can take place.

Although a great deal of progress has been made, significant effort is still being put into the improvement of the overall efficiency of TiO_2 photocatalytic oxidation process. To this end, a wealth of fundamental adsorption and kinetic studies have been carried out to gain a better understanding of the photocatalytic processes with a view to improving photocatalytic efficiencies [9–14].

Most of the reported kinetic studies of TiO_2 photocatalytic oxidation of organic compounds have been described by Langmuir–Hinshelwood kinetic models [3,6,9,13,15]. These models employ the surface concentration/coverage of reactants to describe the reaction rate. However, problems associated with accurately identifying and employing such models often rely on the accurate measurement of the surface concentration/coverage of reactants. Typically, adsorption at TiO_2 surfaces are conducted by employing large surface area TiO_2 nanoparticle slurries [2,11,16–18]. This is done to ensure that measurable amounts of adsorbate will be removed from the solution. The amount of adsorbed species is usually calculated by measuring the decrease in concentration of adsorbate in the solution after separation of the slurry. Apart from the practical problems associated with this approach, there are many uncontrollable factors involved in such a measurement that result in a great difficulty in maintaining desired experimental conditions. The most significant of these is the fact that adsorbate concentration in the bulk solution can change appreciably and rapidly during adsorption. The pH of the solution can also change for some adsorbates due to the deprotonation/protonation during adsorption. As a consequence, maintaining certain experimental conditions

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* Corresponding author. Tel.: +61-7-5552-8261; fax: +61-7-5552-8067.
E-mail address: h.zhao@mailbox.gu.edu.au (H. Zhao).

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is very difficult and the adsorption value would be different from that under specified conditions.

In this study, we propose an ex situ photoelectrochemical method to accurately quantify the adsorption of organic compounds on the TiO_2 surface. The method involves two steps. A TiO_2 porous film electrode is immersed in the sample solution containing the adsorbate for a given time to allow adsorption. The electrode is then removed from the sample solution into a separate detection solution containing only supporting electrolyte to perform the photoelectrochemical measurement. The photoelectrochemical charge generated from photoelectrochemical oxidation of the adsorbate was used to quantify the extent of surface coverage. Immobilisation of TiO_2 onto a conducting substrate makes the application of photoelectrochemical techniques possible. The adsorbate concentration depletion and pH changes in the bulk solution caused by the adsorption are decreased to negligible proportions due to a large solution volume/electrode area ratio. The high sensitivity of electrochemical techniques ensures accurate measurement even at very low surface coverage. Phthalic acid was used as the adsorbate to test the method due to its known strong adsorption onto TiO_2 surfaces [19]. The adsorption isotherm of phthalic acid was obtained and the binding constant was determined according to the Langmuir adsorption model. The effect of pH on phthalic acid adsorption was also investigated.

2. Experimental section

2.1. Materials

Indium tin oxide (ITO) conducting glass slides (8 Ω per square) were commercially supplied by Delta Technologies Limited (USA). Titanium butoxide (97%, Aldrich) and potassium hydrogen phthalate (AR, Aldrich) were used as received. All other chemicals were of analytical grade and purchased from Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18 MΩcm).

2.2. Preparation of the porous TiO_2 film electrode

Aqueous TiO_2 colloid was prepared by hydrolysis of titanium butoxide according to the method described by Nazeeruddin et al. [20]. The resultant colloidal solution contains 60 g dm^{-3} of anatase TiO_2 nanocrystals with particle size ranging from 8 to 10 nm. ITO glass slides were used as the electrode substrate and were pre-treated by washing in turn with detergent, water, chromic acid washing solution, water and ethanol. Caution was taken to avoid the damage of ITO layer by the acidic dissolution during the treatment. The contact time of the substrate with the chromic acid was <30 s, and then the substrate was immediately rinsed with water. The conductivities of the substrate were examined before and after the treatment. No measurable conductivity change was observed. After pre-treatment, the ITO slide was dip-coated in the TiO_2 colloidal solution. The coated electrodes were then calcined in a muffle furnace at 450 °C for 30 min in air. The thickness of the anatase TiO_2 nanoporous film was approximately 1 μm, measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

2.3. Apparatus and methods

All photoelectrochemical experiments were performed at 23 °C in a three-electrode electrochemical cell with a quartz window for illumination. The TiO_2 film electrode was employed as the working electrode and placed in an electrode holder with ca. 0.65 cm^2 left unsealed to be exposed to the solution for illumination and photoelectrochemical reaction. A Ag/AgCl (3 M NaCl) electrode and platinum mesh were used as the reference and auxiliary electrodes, respectively. A voltammograph (CV-27, BAS) was used for application of potential bias in the photoelectrolysis experiments and linear potential sweep experiments. Potential and current signals were recorded using a Macintosh computer (7220/200) coupled to a Maclab 400 interface (AD Instruments). Illumination was carried out using a 150 W xenon arc lamp light source with focusing lenses (HF-200w-95, Beijing Optical Instruments). To avoid the sample solution being heated-up by the infrared light, the light beam was passed through an UV-band pass filter (UG 5, Avotronics Pty. Limited) prior to illumination of the electrode surface.

The linear potential sweep experiments were carried out at the indicated scan rates with a light beam of constant intensity continuously illuminating the porous TiO_2 working electrode. With the photocurrent transient experiments, a constant potential bias of +0.20 V was applied to the electrode and the illumination was switched on and off with a manual shutter.

The measurement of phthalate adsorption was conducted in two steps. The pre-adsorption of phthalic acid was performed by immersing the TiO_2 coated electrode in sample solutions containing 0.1 M $NaNO_3$ and various concentrations of potassium hydrogen phthalate for 30 min. After pre-adsorption, the electrode was removed from the sample solution and immediately washed with 0.1 M $NaNO_3$ before it was transferred into a blank solution (0.1 M $NaNO_3$), where the illumination of electrode was switched on and the adsorbed phthalate molecules were degraded. The photocurrent response resulted from the degradation of pre-adsorbed phthalate molecules were recorded under +0.20 V applied potential bias and the illumination of 6.6 mW cm^{-2} light intensity. The total charge was obtained by integrating the photocurrent during the degradation period with the background charge deducted.

All experiments were carried out using unbuffered electrolyte (0.1 M $NaNO_3$). The pH of the solution was adjusted with nitric acid or sodium hydroxide solution and was closely monitored during the experiment with a pH meter.

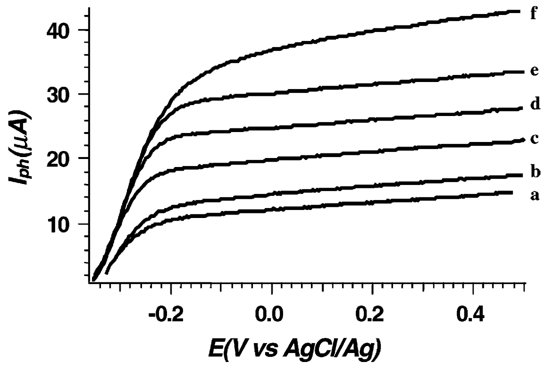

Fig. 1. Voltammograms of the porous TiO_2 electrode in 0.1 M $NaNO_3$ solution of different potassium hydrogen phthalate concentrations at pH 4.0, at 6.6 mW cm^{-2} light intensity and at scan rate 10 mV/s: (a) no potassium hydrogen phthalate; (b) 10 μM; (c) 30 μM; (d) 50 μM; (e) 75 μM; (f) 125 μM.

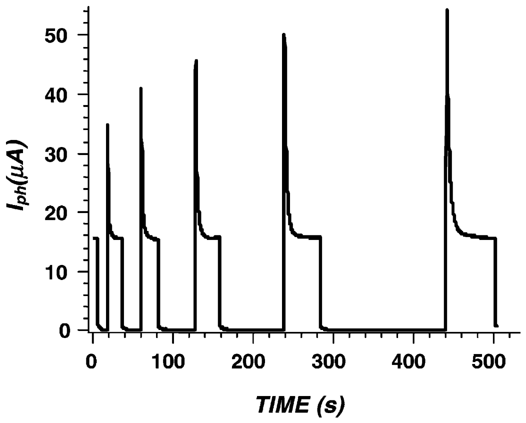

Fig. 2. The in situ transient photocurrent–time profile for different pre-adsorption time, in a solution of 10 μM potassium hydrogen phthalate and 0.1 M $NaNO_3$ at pH 4.0.

3. Results and discussion

3.1. Applied potential bias for photoelectrolysis

The effect of applied potential bias on the photoelectrochemical oxidation of phthalic acid was first investigated. The photocurrent-potential characteristics of the electrodes were obtained in the presence and absence of phthalate by linear sweep voltammetry at a rate of 10 mV/s between −0.30 and 0.50 V versus Ag/AgCl (Fig. 1). The result shows that the photocurrent increases linearly with the potential bias in the low potential region and then reaches saturation. This is similar to the photocurrent–potential relationship obtained from a porous TiO_2 electrode in a methanol solution as discussed in our previous work [21]. Such photocurrent–potential relationship may be explained as follows. For a given light intensity, the concentration of photogenerated electron–hole pairs (or the rate of electron–hole pair generation) is constant. The current, the actual rate of electrons reaching the back contact, depends on two factors, which are the electron transport in the film and the photohole capture process at the TiO_2–solution interface, both of which are vital to the suppression of electron–hole pair recombination. Before the photocurrent reaches saturation with respect to potential, the electron transport across the film is the rate-determining step, as a result, a linear relationship is obtained related to the film resistance. When the rate of the electron transport is increased by increasing the applied potential, the rate of reduction of the photogenerated hole becomes the dominant factor resulting in photocurrent saturation. In this study, a +0.20 V potential bias was selected for all subsequent experiments. This was chosen such that the potential bias was sufficient to suppress the recombination of photoinduced electron–hole pairs but not so positive as to lead to direct electrochemical oxidation of water at the ITO substrate, which complicates the adsorption measurements.

3.2. In situ transient photocurrent response

Under a constant applied potential bias, a photocurrent spike can be observed from a TiO_2 porous film electrode when the illumination was turned on. This phenomenon has been reported for photoelectrochemical oxidation of oxalate at TiO_2 porous film electrodes, which is related to the consumption of adsorbed oxalate rather than double layer charging and discharging process [22,23]. To clarify what causes this phenomenon, in situ light-on and -off experiments were conducted in phthalic acid solution. Fig. 2 shows the transient photocurrent responses obtained at +0.20 V applied potential with different light-off time duration in a 0.10 M $NaNO_3$ solution (pH 4.0) containing 10 μM potassium hydrogen phthalate. A sharp photocurrent spike was observed immediately after the light was switched on which then decayed back to a steady photocurrent. The result also revealed that the magnitude of the photocurrent spike and spike area increased as the time of the dark period increased. The steady-state photocurrent was independent of the time of dark period. The transient response of photoelectrodes has long been observed and studied. Though the transient response often reflects the charging or discharging of space charge layer and electric double layer capacitance [24], nevertheless, the transient photocurrent observed here is unlikely due to the charging or discharging of capacitance. It is likely due to Faradic photoelectrochemical process caused by degradation of adsorbed phthalate. This is evident from the fact that the time domain of the transient observed was much longer than the normal capacitance response of space charge layer and electric double layer. Further more, the spike area was found to be dependent on the non-illumination time length and on the phthalate concentration, which is, in turn related to the surface coverage of phthalate. This prompted us to quantitatively measure adsorption by this photoelectrochemical method.

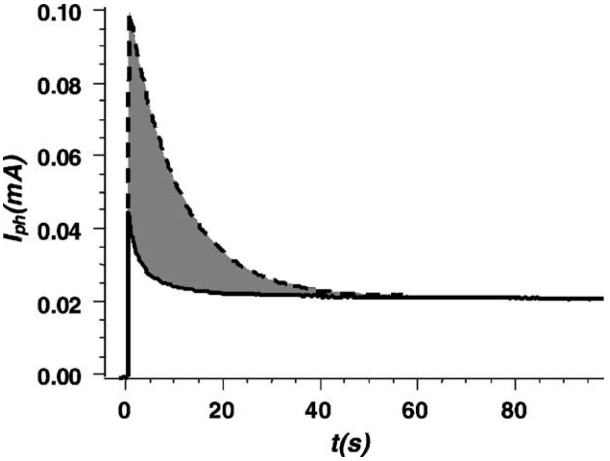

Fig. 3. The ex situ transient photocurrent–time profile of an anatase TiO_2 nanoporous electrode in 0.1 M $NaNO_3$ after it was: (- -) ex situ pre-adsorbed in 5 μM phthalic acid + 0.1 M $NaNO_3$ solution at pH 4.0 for 8 min and (—) an electrode with no pre-absorbed phthalic acid.

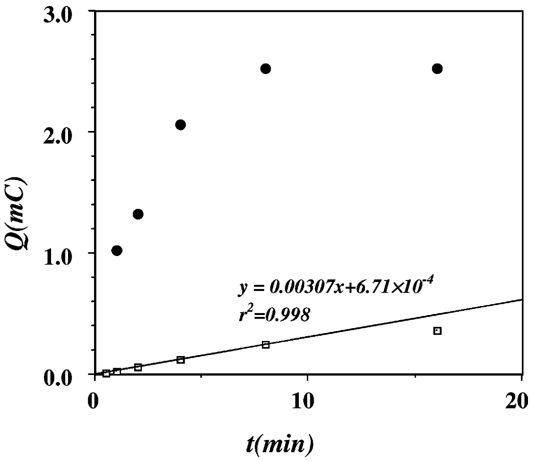

Fig. 4. The charge dependence on ex situ pre-adsorption time after pre-adsorbed in 0.1 M $NaNO_3$ solution containing different concentrations of phthalic acid at pH 4.0: (☐) 2.5 μM, (●) 40 μM.

3.3. Measurement of phthalate adsorption

3.3.1. Quantitative relationship

To avoid the interference of the photoelectrochemical degradation of phthalic acid from bulk solution on the adsorption measurement, an ex situ photoelectrochemical measurement method was proposed. The TiO_2 coated electrode was firstly immersed in the sample solutions containing different concentration of phthalic acid to complete the pre-adsorption and then transferred to a blank electrolyte solution, where photoelectrolysis was performed. Fig. 3 shows the typical photocurrent–time profiles obtained from the electrodes that pre-adsorbed with a phthalic acid solution and a blank electrolyte solution. It can be seen that the photocurrent decayed with time and then reached a steady value, which was due to the oxidation of water [21]. It is noted that the blank photocurrent obtained from the electrode pre-adsorbed in blank electrolyte solution was purely due to the oxidation of water. The photocurrent obtained from the electrode pre-adsorbed in phthalic acid, however, consists of two current components, one due to photoelectrochemical oxidation of adsorbed phthalic acid, and the other due to the oxidation of water, which is the same as the blank photocurrent. Our experimental results showed that the blank photocurrent was essentially constant for the given set of experimental conditions. For a given time period, the charge passed for both the cases can be obtained by integration of the photocurrent and blank photocurrent. The charge difference between the two cases is the net charge due to the photoelectrochemical oxidation of the adsorbed phthalic acid, which is indicated as the shaded area in Fig. 3.

Fig. 4 shows the relationship between the net charge and the ex situ pre-adsorption time at a given phthalic acid concentration. It was found that the adsorption equilibrium was reached in <10 min at relatively high concentration of phthalic acid (40 μM). At low adsorbate concentration (2.5 μM), the net charge linearly increases with pre-adsorption time and then levels off, indicating the adsorption equilibrium. Under such adsorption conditions, the linear relationship between the net charge and adsorption time implies the relationship between net charge and adsorption amount is also linear. This is because the adsorption process is controlled by diffusion under low adsorbate concentration and low surface coverage, and according to Fick's law the adsorption amount should be proportional to the adsorption time. In fact, the linear relationship between the net charge and amount of adsorption obtained here is a direct reflection of Faraday's law.

3.3.2. Adsorption thermodynamics

In order to measure the adsorption isotherm, the time required to reach the adsorption equilibrium under various phthalic acid concentrations was investigated. The results demonstrated that the adsorption equilibrium can be reached within 30 min of ex situ pre-adsorption for all concentrations investigated. After pre-adsorption in a phthalic acid sample solution, TiO_2 porous film electrode was transferred to a 0.1 M $NaNO_3$ blank solution to perform photoelectrochemical measurement. The net charges, Q, were measured by integrating the net photocurrent within the degradation period. As demonstrated in Fig. 4, the net charge, Q, is directly proportional to the amount of adsorbed phthalic acid. Fig. 5 shows the relationship between the net charge (amount of adsorbates) and the concentration of phthalic acid in the sample solution, hence we have established an adsorption isotherm where the amount of adsorbed material is represented by the net photoelectrochemical charge.

The Langmuir adsorption model has been commonly employed to study the adsorption behaviour of organic compounds on metal oxide surfaces [11,25]. Assuming monolayer adsorption, the surface coverage, θ, can be

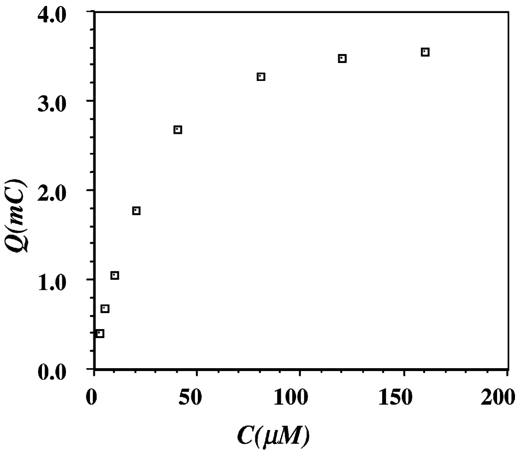

Fig. 5. The dependence of electric charge passed after ex situ pre-adsorbed for 30 min in 0.1 M $NaNO_3$ containing different concentrations at pH 4.0 on the concentration of phthalic acid.

written as:

$$\theta = \frac{Q}{Q_{\max}} \quad (1)$$

where Q is the net charge due to the photoelectrochemical oxidation of adsorbates and $Q_{\max}$ the maximum net charge at 100% surface coverage.

The Langmuir isotherm equation can then be written as:

$$\frac{C}{Q} = \frac{1}{Q_{\max}}C + \frac{1}{Q_{\max}}\frac{1}{K} \quad (2)$$

where C is the bulk concentration of adsorbate in the sample solution and K the adsorption equilibrium constant. An assumption of this approach is that there is no significant change in the bulk concentration of the adsorbate during the adsorption process. In our case, this assumption is met due to the large solution volume to the electrode area ratio.

Treating the data obtained in Fig. 5 according to Langmuir model by plotting C/Q against C gives a straight line with $R^2 = 0.998$ (Fig. 6). This implies the adsorption data agrees well with Langmuir adsorption model. The maximum charge, $Q_{\max} = 4.19$ mC, was obtained from the slope of the curve. According to Eq. (1), the surface coverage θ can be calculated after the $Q_{\max}$ is determined. The adsorption equilibrium constant, $K = 4.0 \times 10^4\ \mathrm{M}^{-1}$ was obtained from the ratio of the slope to the intercept of the curve (see Eq. (2)). The K value obtained by this photoelectrochemical method was close to that of phthalic acid adsorption at TiO_2 (Degussa p25) obtained by Moser et al. [19] of $5 \times 10^4\ \mathrm{M}^{-1}$ at pH 3.6. The agreement of adsorption with the Langmuir adsorption model suggests that the molecules form a monolayer coverage.

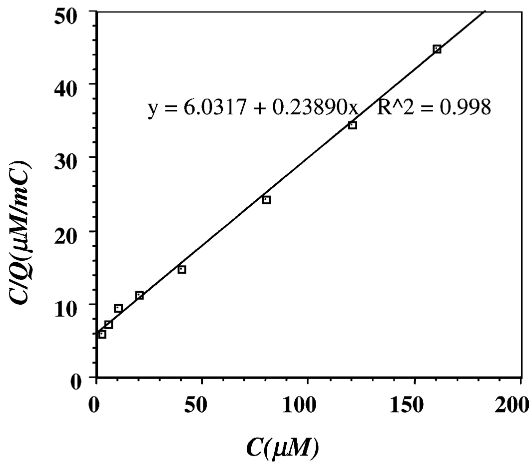

Fig. 6. The fitting of the isotherm to Langmuir adsorption model.

3.4. *Influence of pH on phthalic acid equilibrium adsorption amount*

It is widely accepted that carboxylic groups can coordinate with TiO_2 surface to form surface complexes [17,19,26,27]. This process can be affected by the solution pH since the speciation of both the TiO_2 surface and the phthalate molecules are pH dependent due to protonation/deprotonation. Fig. 7(a) shows the functional group speciation change of the TiO_2 surface (–TiOH surface bound hydroxyl group) with pH as derived from Kormann et al. [28], while Fig. 7(b) shows the species distribution of phthalic acid (H_2Th) with pH, and Fig. 7(c) shows the dependence of the adsorption amount of phthalic acid on pH in sample solution. At pH 4.0, the adsorption reached

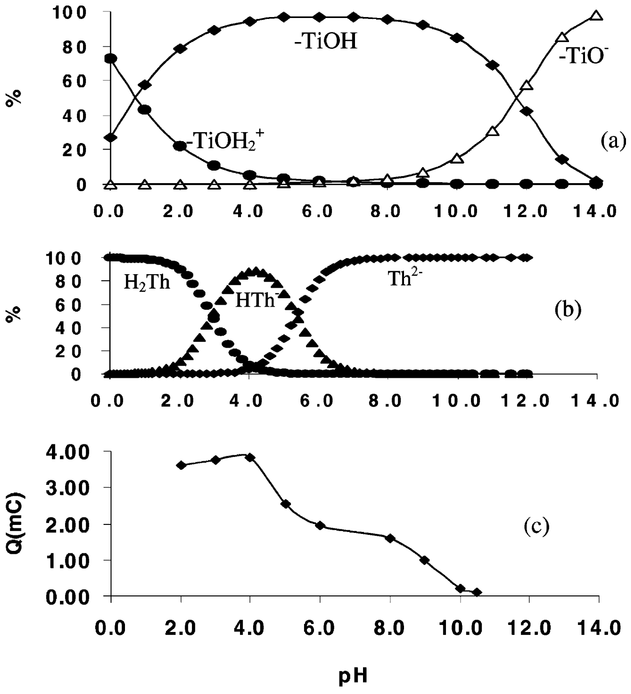

Fig. 7. Comparison of surface speciation distribution of: (a) TiO_2 surface groups (experimental results of Kormann et al. [28]), (b) speciation distribution of phthalic acid in solution, and (c) the adsorption dependence of phthalic acid on pH, adsorption was carried out in 0.1 M $NaNO_3$ containing 160 μM phthalic acid for 30 min.

maximum, which coincides with the maximum fraction of HTh^-. This implies that HTh^- can be favourably adsorbed to TiO_2 surface. Considering the TiO_2 surface carries positive charges in acidic conditions and HTh^- carries a negative charge, the adsorption seems to benefit from the electrostatic attractive force between them. From pH 4.0 to 2.0 the fraction of HTh^- species in solution dropped significantly, nevertheless, only a slight decrease in the amount of adsorption was observed. Given phthalic acid at pH 2.0 mainly exists in neutral molecule form, electrostatic attraction force between molecular form of phthalic acid and electrode surface is insignificant. Therefore, the adsorption is more likely of chemical bonding nature. The sharp decrease in adsorption quantity from pH 4.0 to 6.0 indicates the HTh^- was more favourably adsorbed on –TiOH than Th^{2-} on –TiOH sites. The adsorption amount remains relatively constant from pH 6.0 to 8.0. It can be seen from Fig. 7(a) that the TiO_2 surface is essentially neutral, the electrostatic attraction or repulsion between adsorbate and TiO_2 surface is insignificant. The significant amount of adsorption within this pH range again demonstrates that the adsorption was specific and Th^{2-} can be chemically bound to the TiO_2 surface. As pH increased from 8.0 to 10.0, the negative charge density of TiO_2 surface was increased. As a consequence, the electrostatic repulsion between Th^{2-} and negatively charged TiO_2 surface was increased. This was obviously detrimental to the adsorption and resulted in a sharp decrease in adsorption amount.

4. Conclusion

In this work, we have established a new adsorption measurement method based on photoelectrochemical oxidation principles. The study of phthalate adsorption has demonstrated the usefulness of the developed method in investigating the adsorption behaviour of adsorbates at semiconductor surfaces. The amount of adsorbate, the surface coverage and the equilibrium adsorption constant can be determined in a simple, rapid, sensitive and accurate manner. To our knowledge, this is the first time such a measurement principle has been used for this type of application. The adsorption dependence of phthalic acid on pH was investigated and well explained by the speciation changes of both the TiO_2 surface and phthalic acid with pH. It was found that the adsorption of phthalic acid onto TiO_2 surface at different pH can be attributed to two different interactions, one is specific adsorption that involves chemical bonding and the other is electrostatic interaction between the different forms of TiO_2 and phthalic acid.

The proposed photoelectrolysis method has been demonstrated to be a useful tool for adsorption studies of organic compounds. The photocurrent decay of the adsorbed organic compound also provides a lot of information about the photocatalytic oxidation kinetics of the adsorbed organic compounds at TiO_2 porous film. Further investigation into this area is in progress.

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