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Comparison of photocatalytic degradation kinetic characteristics of different organic compounds at anatase TiO_2 nanoporous film electrodes

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Abstract

Photoelectrochemical method was adopted to investigate the photocatalytic oxidation of different organic compounds. It was found that at the anatase TiO_2 nanoporous electrode, the potential bias changes the rate-determining step from electron migration in the film at low potentials to photohole capture at relatively high potentials. When the applied potential bias is sufficient, the steady state photocurrent obtained reflects exclusively the rate of photohole capture at TiO_2 surface. Under such conditions, the photocatalytic degradation of various organic compounds with different chemical structures was studied.

At very low concentrations, the linear increase of steady state photocurrent with the concentration was observed for all compounds investigated, due to the mass transfer limitation, although the number of electron needed for complete mineralization of these compounds differs markedly. It was demonstrated that the substrate molecules that reaches the electrode surface have been exhaustively mineralized under mass transfer-controlled conditions regardless of their chemical nature.

At high concentration, substrate molecules (or intermediates) are accumulated on the surface (or in the reaction zone). As a result, the steady state photocurrent deviated from the linear relationship. Under such conditions, the interaction of substrate molecules and/or partially degraded intermediates with TiO_2 determines the overall photohole capture rate. The differences in photohole capture rate among different organic compounds were observed. The kinetic characteristics of different organic compounds at high concentrations were also explained based on the structural differences.

Keywords: Photoelectrochemistry; Photocatalysis; TiO_2; Anatase; Nanoporous film

1. Introduction

In the past two decades, TiO_2 photocatalysis has been widely investigated for degradation of organic compounds by means of light-induced oxidation at the TiO_2/liquid interface [1–3]. Although the notable progress has been made, the light efficiency is low [2] and many fundamental aspects involved in the photocatalytic oxidation process still remained unclear.

To date, most of published research articles in this field have focused on the study of photocatalytic behaviours of one or one type of organic compounds. The photocatalytic behaviours of different compounds may have been studied, but often under different conditions or by different methods. This makes it very difficult to draw conclusive information from these reports that can be used as a general guidance to improve the system performance due to the incomparability of the reported data. This is especially true when the studies are carried out in a TiO_2 suspension/slurry system, where the complexity involved makes it impossible to control the experiment under desired conditions [4–9].

Immobilisation of TiO_2 particles onto conducting substrate enables the application of electrochemistry techniques. The introduction of electrochemical technique into a photocatalytic oxidation process, namely, photoelectrochemical catalytic oxidation, has been employed to improve the

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light efficiency since the recombination of photogenerated electrons/holes can be suppressed by applied potential bias [10–12]. More importantly, this approach creates a new way of studying the fundamentals of photocatalytic processes. The method has been proven to be effective in obtaining thermodynamic and instant kinetic information of photocatalytic processes in a simple, rapid and accurate manner [4–7,12]. This is partially because the system configuration allows for the investigation of a specific process without the influence of others. For example, with the photoelectrochemical approach, photocatalytic oxidation and reduction half reactions take place at two different electrodes. The physical separation of the two half reactions enables us to focus on the oxidation process of interest without the interference by the reduction process. This overcomes the interference of electron removal kinetics by oxygen, which presents a serious problem in the slurry system where the rate of overall photocatalytic reaction is often controlled by the photoelectron removal process. In addition, photoelectrochemical approach allows the application of potential bias, which can be used to manipulate the rate-determining step of the overall photocatalytic process [4,5]. Furthermore, with photoelectrochemical approach, the photocurrent resulted from the photocatalytic oxidation can be readily measured and it can be used to express the instant rate of reaction. More importantly, it directly reflects the photoefficiency of the photocatalytic system regardless of the type of organic compounds and the degree of their mineralization. This contrasts the conventional kinetic study method in that usually the rate of reactant disappearance is adopted to express the photocatalytic reaction rate [2,8,9]. The use of reactant disappearance rate as the expression of photocatalytic reaction rate makes the comparison of photocatalytic reaction rate of different organic compounds difficult due to the uncertainty of photodegradation degree during the progression of photodegradation reaction.

There have been studies where immobilised TiO_2 porous film and electrochemical techniques were employed. However, the purpose of these studies mainly focused on the enhancement of photocatalytic degradation efficiency by applying potential bias [10,11,13,14] and photoelectrochemistry as a means to study photocatalytic degradation processes has yet been explored.

The main objective of this study is to investigate the relationships between the characteristics of photocatalytic kinetics and the chemical structures of the substrate. In order to achieve this, the photocatalytic behaviors of different organic compounds were systematically characterized under the same experimental conditions at the anatase nanoporous TiO_2 film electrodes. Three different groups of organic compounds were selected as model compounds for this study. These are: weakly adsorbed compounds (methanol and glucose), strongly adsorbed aliphatic compounds (formic acid, oxalic acid, malonic acid, succinic acid and glutaric acid) and strongly adsorbed aromatic compounds (phthalic acid and salicylic acid).

2. Experimental

2.1. Materials

Indium tin oxide conducting glass slides (ITO, 8 Ω/square) were purchased from Delta Technologies Ltd. (USA). Titanium butoxide (97%, Aldrich), potassium hydrogen phthalate (AR, Aldrich), D-glucose (AR, BDH), formic acid (AR, Ajax Chemicals), oxalic acid (AR, Ajax Chemicals), succinic acid (99%, Sigma), malonic acid (Sigmaultra, Sigma), glutaric acid (99%, Sigma), salicylic acid (AR, Aldrich) and methanol (99%, BDH) were used as received. Other chemicals used were of analytical grade and purchased from Aldrich unless otherwise stated. All solutions were prepared using high purity deionised water (Millipore Corp., 18 MΩ cm). Two different types of concentration units were used in the study, one is molar concentration and the other is equivalent concentration. The latter is defined by multiplying the molar concentration with the electron transfer number for the complete mineralization of a specific compound.

2.2. Preparation of porous TiO_2 film electrodes

Aqueous TiO_2 colloid was prepared by hydrolysis of titanium butoxide according to the method described by Nazeeruddin et al. [15]. The resultant colloidal solution contains $60\,g\,dm^{-3}$ of TiO_2 solid and the particle size was 8–10 nm. Carbowax (30%, w/w based on the solid weight of the TiO_2 colloid) was added to increase the porosity of the final TiO_2 film and the resultant colloid was used for the fabrication of nanoporous TiO_2 film on ITO slides. The details for the pretreatment of ITO slides was published elsewhere [6]. After pretreatment, the ITO slides were dip-coated in the TiO_2 colloidal solution. The coated electrodes were then calcined in a muffle furnace at 500 °C for 30 min in air. The resultant film was composed of pure anatase phase as confirmed by X-ray diffraction. The thickness of the film was about 1.0 μm as measured with a surface profilometer (Alpha-step 200, Tencor Instrument).

2.3. Apparatus and methods

All experiments were performed at ca. 23 °C in a three-electrode electrochemical cell with a quartz window for illumination. TiO_2 film electrode was employed as a working electrode that was mounted to a special holder with about $0.65\,cm^2$ left unsealed to be exposed to the solution for illumination and photoelectrochemical reaction. A saturated Ag/AgCl electrode and a platinum mesh were used as the reference and the auxiliary electrodes, respectively. To eliminate the influence of solution resistance, 0.1 M $NaNO_3$ was chosen as the supporting electrolyte. A voltammograph (CV-27, BAS) was used for application of potential bias in the phototransient experiments and linear potential sweep experiments. Potential and current signals were sampled with a Macintosh computer (7220/200) via an interface (Maclab

400, AD Instruments). The illumination was carried out using a 150 W xenon arc lamp light source with focusing lenses (HF-200w-95, Beijing Optical Instruments). Light intensity was measured with a UV-irradiance meter (UVA, Instruments of Beijing Normal University). In the photocatalytic oxidation experiment the pH of the solution was maintained at ca. pH 4.0 and monitored with a pH meter. 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. Ltd.) prior to illuminating the electrode surface.

3. Results and discussion

3.1. *Effect of potential bias*

It has been well accepted that the application of an appropriate potential bias to a TiO_2 porous film electrode during the photocatalytic oxidation can suppress the electron–hole pair recombination [10–12]. We have demonstrated that the mechanism for suppression of the recombination of photogenerated electron–hole pairs at a nanoparticulate semiconductor electrode is different from a conventional bulk semiconductor electrode [5,16]. This is mainly due to the particulate semiconductor film electrode cannot sustain the formation of space charge layer as does in a conventional bulk semiconductor electrode [5,16]. Hence, the effect of the applied potential bias on the photocatalytic process at the two types of electrodes differs remarkably from one and the other [5,16].

In order to investigate the influence of the potential bias on the rate of the overall photocatalytic reaction, linear sweep voltammograms of the pure anatase nanoporous TiO_2 film electrode were recorded in solutions containing different organic compound. The organic compounds studied here include methanol, glucose, formic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, phthalic acid and salicylic acid.

Fig. 1 shows a set of typical voltammograms obtained from a 0.1 M $NaNO_3$ solution containing different concentrations of glucose at pH 4.0. It should be noted that the characteristics of the voltammograms obtained from different organic compounds listed above were very similar to the case presented in Fig. 1. In all the cases, even in the absence of organic compounds the photocurrents increased linearly with the potential bias at low potentials and then saturated at more positive potentials. This is because the application of potential bias altered the rate-limiting step of the overall photocatalytic process [4].

The electron transfer in the photocatalytic oxidation process involves two major processes. One is the electron transport in the semiconductor film and the other is the electron injection at the interface (photohole capture). At low potentials the electron transport in the film controls the overall photocatalytic process, as a result, the photocurrent increases with potential. Since for a given compound, at a given concentration, the rate of electron injection or photohole capture (determined by the concentrations of photohole and organic compounds on TiO_2 surface) is constant, therefore, the photocurrent is saturated with respect to potential bias. Overall, to maintain the progression of reaction at interface, both photoelectrons and photoholes must be removed in time. Otherwise, the build-up of either charge carrier would accelerate the rate of photoelectrons/holes recombination, resulting in a decrease in the overall reaction rate.

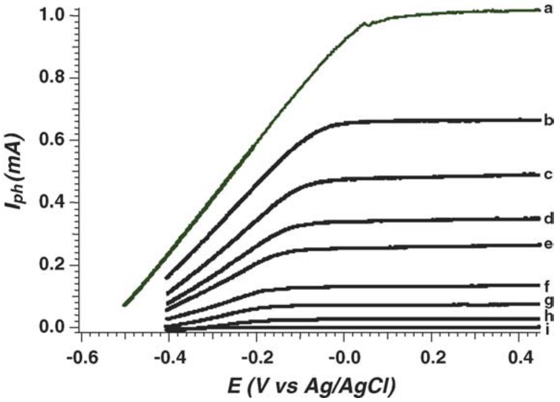

Fig. 1. Voltammograms of the porous film electrode in solutions of 0.1 M $NaNO_3$ containing different concentration of glucose at 6.6 mW cm^2 light intensity and a scan rate of 5 mV. The glucose concentration (a) 450 mM, (b) 50 mM, (c) 10 mM, (d) 3 mM, (e) 1.5 mM, (f) 0.4 mM, (g) 0.1 mM, (h) 0.0 mM, (i) 0.0 mM in dark.

The primary function of the applied potential bias in the case of a particulate semiconductor film electrode is to facilitate the freed photoelectrons transport across the semiconductor film to reach the conducting ITO substrate and the external circuit [5]. Once the rate of electron transport inside the film reaches the level comparable to the rate of photohole capture at TiO_2/solution interface, the photocurrent is saturated. Under such conditions the overall reaction is controlled by the photohole capture at the interface. This means that we can select an appropriate potential bias (e.g. +0.30 V versus Ag/AgCl) to ensure that the overall reaction kinetics is controlled by the interface reactions rather than by the electron transport across the semiconductor film [5]. This enables us to focus specifically on the kinetics of photohole capture process by different organic compounds.

3.2. *Effect of substrate concentration*

The effect of concentration of the various organic compounds on the steady state photocurrent was investigated. The steady state photocurrent (I_{sph}) was measured for each organic compound at different concentrations. The potential bias applied was +0.30 V versus Ag/AgCl. As described in the previous section, the steady state photocurrent obtained under such conditions reflects the kinetics of photohole capture processes at the electrode/solution interface. Figs. 2–4 show the relationships between the steady state photocurrent (I_{sph}) and the molar concentration (C) for different organic compounds under the same experimental conditions.

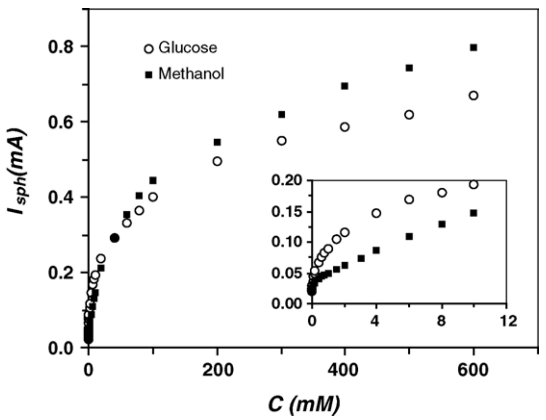

Fig. 2. The plot of I_{sph} vs. C for glucose and methanol.

Fig. 2 shows the I_{sph}/C curves obtained from the oxidation of methanol and glucose. These organic compounds are known to be weakly adsorbed to TiO_2 surface [4,12,17]. The results showed that the steady state photocurrent increased monotonically with substrate concentration. Detailed examination of the results revealed that the I_{sph} increased linearly with concentration up to 0.5 mM. The liner response obtained indicates the overall photocatalytic reaction was under diffusion control at concentration below 0.5 mM. When the concentration was further increased, the I_{sph} deviated from the linear response due to the fact that diffusion no longer controls the overall process. After diffusion control stage, the monotonic increase of I_{sph} with substrate concentration suggests that the interaction of these compounds (or their partial-degraded intermediates) with the TiO_2 surface do not inhibit the photohole capture process and the increasing amount of these compounds and their partial-degraded intermediates in the reaction zone facilitates the photohole capture process. The weak interaction of these compounds and/or their partial-degraded intermediates with TiO_2 surface is responsible for the behavior.

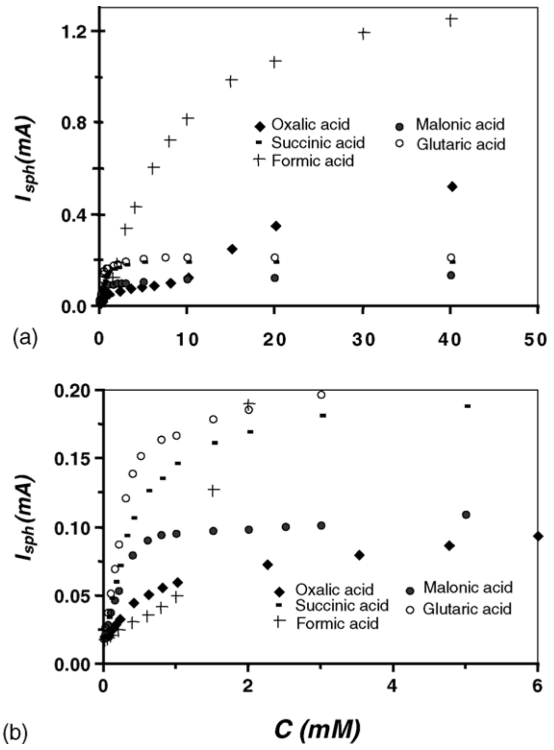

Fig. 3. The plot of I_{sph} vs. C for formic acid and dicarboxylic acids.

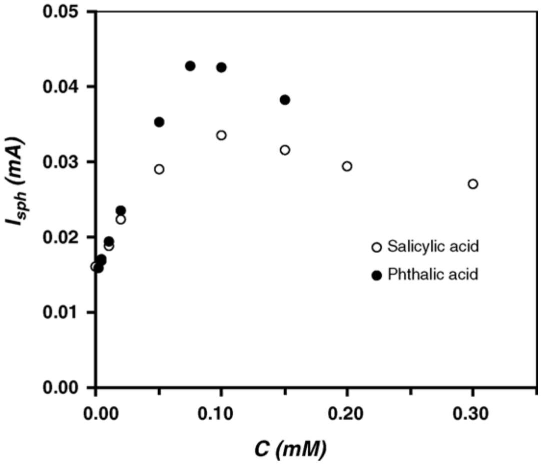

Fig. 4. The plot of I_{sph} vs. C for phthalic acid and salicylic acid.

Fig. 3 shows the I_{sph}/C relationships for a group of aliphatic acids including formic acid, oxalic acid, malonic acid, succinic acid and glutaric acid, which have one or two carboxyl functional groups. These acids are known to be strongly adsorbed at TiO_2 surface [18–20]. It can be seen that for this group of compounds, the characteristics of the I_{sph}/C curves differ markedly from those shown in Fig. 2. Also, the characteristics of the I_{sph}/C curves are different even among the group of compounds.

Complete mineralization of the simplest aliphatic acids such as formic acid and oxalic acid involve the least number of electrons (i.e. $2e^-$), and degradation steps and intermediates. The I_{sph}/C curves obtained from these simple acids exhibited characteristics of a multi-wave shape, which differs from all other compounds investigated. The I_{sph} increased linearly in very low concentration range and then leveled-off at slightly higher concentrations. This was followed by a further increase in I_{sph} at medium concentrations before leveling-off again at high concentrations. The linear increase in I_{sph} at low concentrations is due to the substrate diffusion limitation and the subsequent plateaus and increase with concentration is probably related to the interaction of TiO_2 surface with these compounds (or their intermediates).

Larger aliphatic acids (malonic acid, succinic acid and glutaric acid) involve larger number of electron transfer, more steps and intermediates during their complete mineralization process. I_{sph} increased linearly at very low concentrations and then leveled-off at slightly higher concentrations (see Fig. 3). A second wave of I_{sph} increase and level-off was still observed for malonic acid but not for others. Interestingly, the magnitude of the first plateau I_{sph} obtained at medium concentrations increased from oxalic acid to glutaric acid. This will be further discussed in the next section.

Fig. 4 shows the I_{sph}/C curves of aromatic compounds. Two model compounds selected for this study are phthalic acid and salicylic acid, both having two functional groups and are known to be strongly adsorbed to TiO_2 surface [18,21]. The characteristics of I_{sph}/C curves for the organic compounds of this category were found to be different to all compounds investigated in the previous sections. It is apparent that the I_{sph} increased linearly at very low concentration within a very narrow concentration range and then decreased (instead of leveling-off) as the concentration increased. Furthermore, the concentration range in which this occurred was much lower than for the other compounds.

3.3. *Characteristics of photocurrent responses under equivalent substrate concentration*

The magnitude of I_{sph} is mainly determined by two factors—the rate of photohole/photoelectron generation and the rate of photohole capture by electron donors at the electrode surface. For a given TiO_2 electrode at a given light intensity, the former is fixed. The latter, however, is influenced by the availability of electron donors at the electrode surface and the interaction between the TiO_2 surface and the electron donors (organic compounds). Without doubt, under sufficient potential bias the difference in the magnitude of I_{sph} is the result of the competition between the photoelectron/photohole recombination process and the photohole capture process. For a given TiO_2 electrode, the intrinsic characteristics of the semiconductor for photoelectron/photohole recombination are fixed. Only through the photohole capture reaction by organic compounds at the electrode surface can the rate of photoelectron/photohole recombination be further regulated. Therefore, the value of I_{sph} solely reflects the rate of photohole capture at TiO_2 interface, which is determined by the availability of electron donors (organic compounds) at TiO_2 surface, their interaction with the TiO_2 surface, the nature of their intermediates and the molecular steric suitability of adsorbed form of organic compounds to capture photoholes.

As presented in the previous sections, in all the cases in low molar concentration range, the I_{sph} increased linearly with molar concentration. For the organic compounds investigated above, the number of electrons required for complete mineralization of these compounds varies from $2e^-$ to $30e^-$, and the number of steps and intermediates involved differ greatly from one to another. Clearly, the linear increase of I_{sph} with molar concentration indicates that the availability of electron donors at electrode surface is a control factor of the overall photocatalytic oxidation process. A question raised is whether under such conditions different organic compounds reaching the electrode surface are completely mineralized. This issue needs to be addressed first.

According to the semiempirical treatment of steady state mass transfer method [22], under diffusion-controlled conditions, the limiting steady state photocurrent can be given by:

$$I_{sph} = \frac{nFADC}{\delta} \tag{1}$$

where, n is the number of electrons transferred for the complete mineralization of organic compounds, F is the Faraday constant, A is the surface area of the electrode, D and δ refer to the diffusion coefficient of the substrate and the thickness of the effective diffusion layer, respectively, and C is the bulk concentration of the compound.

If we define a new quantity $C_{eq} = nC$, then, Eq. (1) predicts that under diffusion-controlled conditions, if all the compound molecules reaching the electrode surface are stoichiometrically mineralized, a linear I_{sph}/C_{eq} relationship with a slope of FDA/δ would be held for all compounds. It should be noted that at the same C_{eq}, the photohole demand [4–7,12] is the same for different organic compounds regardless of their chemical identities, which is why such a technical term is introduced.

If we define an arbitrary flux index as $\text{Flux}^{in} = ADC_{eq} = nADC$, Eq. (1) can therefore be written as:

$$I_{sph} = \frac{F \times \text{Flux}^{in}}{\delta} = k\text{Flux}^{in} \tag{2}$$

Under diffusion controlled conditions, if we assume δ is same for all compounds under different Flux^{in} and the reaction takes place stoichiometrically, then for a given electrode $k = F/\delta$ is a constant regardless of chemical structures of the compounds involved. Under these conditions, Eq. (2) predicts a linear relationship between the I_{sph} and Flux^{in}, and the slope, k, should be same for all compounds.

To examine whether under diffusion-controlled conditions the organic compounds reached the electrode surface are completely mineralized, the I_{sph} was plotted against Flux^{in} for a number of organic compounds, whose diffusion coefficient values are available (see Fig. 5). At low effective equivalent flux, for all compounds investigated, the I_{sph}/Flux^{in} can be fitted into a linear equation, $I_{sph} = 0.00373\,\text{Flux}^{in} + 0.0193$ (mA), with R^2 of 0.995. This confirms that all compounds under diffusion-controlled conditions were stoichiometrically mineralized regardless of their chemical structure.

For most of the organic compounds, since their diffusion coefficient values are not available, their steady state photocurrents (I_{sph}) were plotted against equivalent concentrations (C_{eq}) (see Fig. 6). It was found that at very low C_{eq} range, photocurrents obtained from different compounds increased linearly with concentration. More importantly, almost identical slope values were obtained from all I_{sph}/C_{eq} curves. The small variation in the slope values is due to the difference in the diffusion coefficients of different organic compounds. Such results can be obtained only when the real electron transfer number during the photocatalytic process is identical to the theoretical electron number

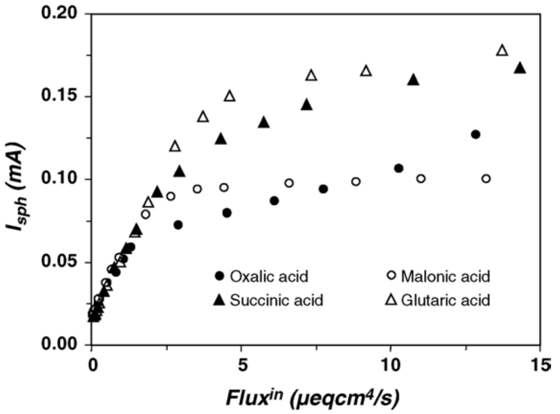

Fig. 5. Dependence of I_{sph} on the equivalent flux index for dicarboxylic acids (the value of D (10^{-5} cm^2 s^{-1}): hydrogen oxalate 0.987, hydrogen malonate 0.845, hydrogen succinate 0.783, hydrogen glutarate 0.7 at pH 4.0 [23]).

required for complete mineralization. In other words, these results indicate that under diffusion control conditions all compounds have been stoichiometrically mineralized and the chemical structures of the substrates are not a decisive factor in the overall photocatalytic oxidation kinetics. These results also suggest that under diffusion control conditions, all reaction intermediates are oxidized before they are able to diffuse away from the electrode surface.

3.4. Further discussion

From the above discussion, under diffusion-controlled conditions regardless of the chemical structure of the organic compounds, all the substrate molecules reaching the electrode surface are completely mineralized. The deviation of I_{sph} from linear response at higher concentrations indicates that molecules reaching the electrode surface are incomplete oxidised. This means that at higher concentrations the supply of substrates at TiO_2 surface is not the controlling step. As shown in the previous sections, for some compounds, high I_{sph} values were obtained at higher concentrations, which suggests that supply of photoholes is not the controlling factor either. Both photoholes and substrate supply at the electrode surface are not limiting at higher concentrations, however, the steady state photocurrent failed to keep up increasing. It also can be seen from Figs. 5 and 6 that the linear ranges obtained are dependent on the chemical nature of the organic compounds. Therefore it can be concluded that the deviation from linearity and the differences in the linear ranges for different organic compounds are resulted from the differences in the interaction of different organic compounds with TiO_2 surface. In addition, the differences in the nature of their intermediates and the differences in the molecular steric orientation suitability of their adsorbed forms to capture photoholes may also contribute to the deviation from linearity.

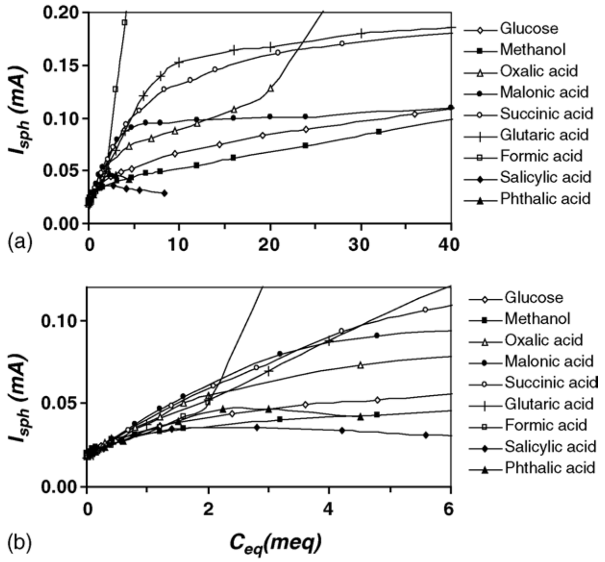

Fig. 6. The relationship between I_{sph} and C_{eq} for different organic compounds in low concentration range (the value of n: glucose 24, methanol 6, oxalic acid 2, malonic acid 8, succinic acid 14, glutaric acid 20, formic acid 2, salicylic acid 28, phthalic acid 30).

Glucose and methanol are not specifically adsorbed on the electrode surface. The photocurrent concentration relationships deviate from linearity as concentration increases, which is an indication of incomplete mineralization of these reactants reaching the reaction zone. However, the photocurrent increases monotonically with concentration, which indicates the intermediates do not poison the electrode, and the electrode surface is fairly uniform to these molecules in the whole concentration range. This probably is an evidence of indirect photohole transfer mechanism in that the photocatalytic oxidation of these compounds is via the heterogeneous reaction between the surface-bonded hydroxyl radical (or surface-bonded holes) and outer-sphere complexes of these compounds. Once their molecules are within the reaction layer, they get chance to react with surface-bonded holes or hydroxyl radicals. The higher the substrate concentration in the bulk solution the more surface-bonded holes (or surface bound hydroxyl radicals) are captured, as a result, more photoelectrons are freed and less recombination occurs. It is also noted that the values of I_{sph} for glucose at medium molar concentrations are higher than those for methanol, while at high molar concentrations the order is reversed. The differences in their molecular sizes, affinities to TiO_2 surface and the current doubling effects of their partial-degraded radicals are probably responsible for this.

Another group of organic compounds studied here are formic acid and aliphatic dicarboxylic acids, which can be specifically adsorbed to TiO_2 surface by forming surface complexes. Kinetically, this group of organic compounds exhibits different photocatalytic behavior to those non-specifically adsorbed compounds (e.g. methanol and glucose), and the specifically adsorbed aromatic compounds (e.g. phthalic acid and salicylic acid).

For the simplest acids such as oxalic acid and formic acid involving the least number of electrons transfer and intermediate steps during mineralization, the I_{sph}/C_{eq} curves exhibit the characteristics of a multi-wave shape. In our previous publication, the adsorption of different dicarboxylic acids were studied [7]. At least three different types of surface complexes were identified, which are strong, medium and weak surface-bonded complexes [7]. According to Regazzoni et al. [21], surface titanium ions at the crystal edges and corners, with fewer coordination positions occupied by O^{2-}, display the highest affinity for adsorbing ligands and the number of these ions is limited. The strong surface-bonded complex can be attributed to adsorption at such sites. The medium surface-bonded complex is responsible for Langmuir adsorption behavior in the medium concentration range and this type of complex accounts for the vast majority of the total adsorption [7]. The weak-bonded complex formed at high concentrations represents a small portion of the total adsorption quantity. Titanium ions from the most stable, perfectly cleaved (0 0 1) and (0 1 1) crystal faces of anatase, which are penta-coordinated to O^{2-} ions and complete their coordination sphere by binding OH^{-}, are responsible for medium and week-bonded surface complexes.

For oxalic acid the first phase of increase in I_{sph} is probably related to the photocatalytic oxidation of strong surface-bonded complex and the second phase of increase in I_{sph} can be contributed to both strong and weak surface complexes. This assignment is based on the appearance of the I_{sph}/C waves in concentration scale and the appearance of different adsorption characteristics in concentration scale [7]. If this assignment is true, the adsorption of medium surface-bonded complex, the majority of adsorption, has little contribution to the capture of photoholes, as evidenced by the I_{sph} level-off in corresponding concentration range. This is a very interesting finding. For formic acid the I_{sph}/C_{eq} relationship is similar to that of oxalic acid, only the concentration range of the first level-off is smaller. Unlike for oxalic acid, the medium surface-bonded complex of formic acid seems less inactive. Given that the binding strength of formic acid is weaker than that of dicarboxylic acids [24], probably this is due to the less binding strength of its medium surface-bonded complex compared with that for oxalic acid, which bring it closer to the cases of glucose and methanol. The fact that glucose and methanol can react at both active sites (edge and corner titanium ions) and the most abundant sites (ordinary surface titanium ions) (as is evidenced by the monotonic increase of I_{sph} with concentration) support this argument. For larger dicarboxylic acids, the first phase of increase in I_{sph}/C_{eq} relationships is similar to that of oxalic acid, and can be assigned to the photocatalytic oxidation of the corresponding strong surface-bonded complexes. The second phase of I_{sph} increase at higher concentrations gradually disappears as the organic molecule becomes larger. This indicates that neither medium surface-bonded complexes nor weak surface-bonded complexes contribute much to the photocurrent response.

Overall, the accumulation of these compounds and their partial-degraded intermediates at the electrode surface does not deteriorate the overall efficiency of the photocatalytic process. The fact that the major surface complexes (at the most abundant sites), accounting for major adsorbed amount, are less photocatalytic active, may be explained by the reactivity differences among the edge, corner titanium sites and the ordinary titanium surface sites. In our previous study, we have found the photocatalytic degradation rate constant for the same adsorbate adsorbed at different types of TiO_2 sites can be six times different [7]. It is due to the difference in reactivity that leads to the oxidation at the more active sites to be preferentially displayed. This finding explains why there were no correlation between photocatalytic oxidation rate and the adsorption amount of strong adsorbates reported by some researchers [8,9,21,25]. Similar explanation was also proposed for the photocatalytic oxidation of salicylic acid in a TiO_2 slurry system [21].

It is noted in Figs. 3 and 5, the magnitude of first wave of I_{sph} plateaus increases from small dicarboxylic acid to larger dicarboxylic acid. Based on the above assignment that the first wave of increase in I_{sph} with concentration is due to the photocatalytic oxidation at the more active sites on TiO_2 surface, the difference in I_{sph} value for the first level-off for different dicarboxylic acids can be easily explained. For a given electrode, the number of this type of active sites is fixed, so is the maximum number of molecules that can access to this type of sites. From oxalic acid to glutaric acid, for the same number of molecules adsorbed, the number of photoholes needed for their mineralization increases, the number of photoholes captured by these molecules increases as well. As a result, the level-off photocurrent is increased. As demonstrated in Fig. 3, approximately same turning-point molar concentrations for the group of compounds (i.e. the concentration where I_{sph}/C curves turn from linearity to first plateau) support this argument.

Similarly, for aromatic compounds the increase in I_{sph} at very low concentration can be attributed to the photocatalytic oxidation of the strong surface complexes adsorbed at corner and edge titanium ions. The major difference from dicarboxylic acids is that the linear increase did not go as high as others, instead, the photocurrent dropped as the concentration was further increased. This is most likely caused by accumulation of the intermediates rather than by the adsorption of compounds. The aromatic intermediates can act as photohole/photoelectron recombination centers due to the special chemical structure of the intermediates (intermediates of benzene ring will keep the conjugate structure through a few stages of degradation) [2]. Evidence of this includes the fact that the I_{sph}/C relationship of phthalic acid at pH 10.0 is the same as that at pH 4.0, but at pH 10.0 there is little phthalic acid adsorption taking place. In addition, for non-specific aromatic adsorbates such as phenol, similar I_{sph}/C relationships were obtained. High local photohole demand for the destruction of benzene ring on TiO_2 surface will cause a longer dwelling time of the intermediates, which facilitates the accumulation. This accelerates the recombination of photoholes and photoelectrons at such active sites due to the recombination center effect of accumulated aromatic intermediates. In contrast to the cases of larger dicarboxylic acids, the aromatic compounds can deactivate the active sites more seriously. This is in agreement with our previous finding that the adsorbed aromatic compounds can distort the fast photocatalytic degradation process [7].

4. Conclusion

At pure anatase TiO_2 nanoporous film electrodes, the photocatalytic degradation kinetics of a number of organic compounds of different chemical structure has been investigated by photoelectrochemical techniques. The kinetic characteristics of these organic compounds have been compared. It has been shown that the steady state photoelectrochemical method is a rapid, direct and effective method for studying the photocatalytic degradation kinetics of various organic compounds under the same conditions. Application of electrode potential allows for studying photocatalytic oxidation kinetics of organic compounds without the influence of electron transport inside the film and the influence of photoelectron removal process as in the case of conventional kinetic study method.

Results demonstrated that under diffusion-controlled condition and very low concentrations, all the structurally different compounds investigated are stoichiometrically oxidized to CO_2 without significant amounts of intermediates leaving the electrode surface. However, the diffusion control concentration ranges and the maximum photohole capture rates at high concentrations varied significantly among different organic compounds. This is caused by the differences in the chemical nature of different organic compounds. For different organic compounds, the differences among their diffusion-controlled concentration ranges (linear ranges) and their photohole capture rates at high concentration have been explained based on the differences in their chemical structures and photohole demand characteristics. The results obtained in this study imply that the photoelectron removal process by oxygen may be not always the limiting step of the overall photocatalytic degradation process in conventional slurry systems, where oxygen is employed as the photoelectron acceptor. For such systems, the photohole capture process by organic compounds can be the limiting step, depending on the chemical structure of organic compounds.

This study demonstrated that the photoelectrochemical method can be used to effectively evaluate the photocatalytic activity and photocatalytic oxidation ability of a photocatalyst. The method can be regarded as a useful tool in selecting a photocatalyst for a particular application.

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