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Photoelectrochemical behaviour of methanol oxidation at nanoporous TiO_2 film electrodes

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Abstract

A study of photoelectrochemical oxidation of methanol at nanoporous TiO_2 film electrodes was carried out. The effect of variables such as applied potential, light intensity, methanol concentration and pH on the photoelectrochemical behaviour was investigated. It was found that the photoresponse was greatly influenced by these factors and a unique photocurrent/potential characteristic of the electrode in solution was observed which was similar to that of the single crystal semiconductor electrode. It was also found that the rate-limiting step for the overall photooxidation process varied depending on potential, light intensity and methanol surface coverage. In low potential region at a given light intensity and methanol concentration the migration of electron across the TiO_2 film is the rate-limiting step. While in the relatively high potential region the interfacial charge transfer was found to be the rate-limiting step. A deviation of onset potential dependence on pH from the Nernstian relationship was also observed, and based on the energy band theory and the existence of deep electron traps an explanation was given. An unusual abrupt increase of photocurrent in strong basic methanol solution was observed, which was attributed to the existence of acidic hydroxyl group on TiO_2 and its stronger adsorption to methanol molecule after its reaction with OH^-, and the higher reactivity of the methanol thus adsorbed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nanoporous TiO_2 film; Methanol oxidation; Photoelectrochemistry

1. Introduction

Over the past two decades, TiO_2, because of its excellent chemical and photochemical stability, and good photoelectrochemical properties, has been the subject of thousands of publications [1–12]. Two areas of study have received particular attention. One involves solar energy conversion where TiO_2 porous electrodes, adsorbed with photosensitizer, are used as light harvesting and light converting components [1–7]; the other is in the environmental sector where TiO_2 particle suspensions or immobilized TiO_2 films are employed to degrade organic wastes in water [8–12]. Together with these application driven studies, a considerable amount of basic theoretical research has been published [13–17], which has facilitated our understanding of the photocatalytic oxidation mechanism of organic substances in TiO_2 nanoparticle suspension systems and charge transfer processes in dye sensitized solar cell.

There are many inherent problems in using the TiO_2 particle suspensions for toxic water remediation. These include the difficulty of separating the photocatalyst from the water, the need to replenish oxygen to keep the degradation reaction going and the low quantum efficiency mainly resulting from inefficient separation of photogenerated charge carriers. Immobilizing the TiO_2 nanoparticles onto glass substrate avoids the filtration step [18–20]. This, however, occurs at the expense of lowering the quantum efficiency even further, due to the diffusion limitations of the organic substances and the decrease in surface area.

By applying an electrochemical potential bias to a TiO_2 film, separation of photogenerated electrons and holes is accelerated and the recombination of photogenerated electrons and holes is suppressed. In addition, the dependence of overall photooxidation rate on the reduction rate of the electron acceptor (e.g. O_2) is eliminated. This approach is therefore a very promising solution to the problems encountered in the particle suspension system. While there have been some published studies and the concept has been justified [21–25], no detailed systematic study has been reported for the photoelectrochemical behaviour of the oxidation of organic substances at the nanoporous film electrode. By contrast, extensive kinetic studies have been published employing TiO_2 particle suspension, covering a wide range

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of organic wastes in water [8–12]. Unfortunately, there are many factors that are not easy to control, such as the light absorbency by TiO_2 particles, the determination of instantaneous substrate concentration (especially for strongly adsorbed species) and the pH change during experiment. Since these factors influence the kinetic behaviour, it is difficult to interpret the experimental results obtained. In addition, kinetic studies in the suspension are very time-consuming.

To overcome these problems, by immobilising TiO_2 nanoparticles onto conducting substrates, photoelectrochemical techniques can be used to study the photocatalytic oxidation of organic substance. This approach has the advantage of being a rapid, in situ method. Above all, it is easy to control the relevant experimental parameters. For example, with a large solution volume to electrode area ratio the concentration of organic species and the pH of the bulk solution can be regarded as constant within a certain time period. Unlike the particle suspension system where the photooxidation and photoreduction reactions take place on the same particles, in the photoelectrochemical experiment they take place at different electrodes. Hence, the influence each on the other can be excluded. All the above features simplify the system and make possible the clarification of the overall photocatalytic process. Essentially both approaches involve the same basic steps, e.g. (1) light absorption and electron transition, (2) spatial charge separation and (3) interfacial charge transfer at a solid/solution interface. Consequently studies of photoelectrochemical oxidation of organic substance would provide more information about the overall photocatalytic process. Research in this respect on the one hand might lead to a new approach for water treatment, which overcomes the existing problems of TiO_2 particle suspension approach; on the other hand it will help gain some insights into the photocatalytic oxidation mechanisms of organic matter.

In this work, a nanoporous TiO_2 film electrode was used as the electrode. Methanol, a well-known radical scavenger and a non-specific adsorbent to TiO_2, was chosen as the electron donor to investigate the photoelectrochemical behaviour of its oxidation at the electrode under a wide range of conditions.

2. Experimental

2.1. Chemicals

Titanium butoxide (97%, Aldrich), methanol (99.8%, BDH), isopropanol (99.8%, BDH), sodium sulphate (99.9%, Beijing Third Chemical Reagent Co.) were used without further purification. Sulphuric acid and sodium hydroxide employed were of analytical grade. Deionised water was used in all solution preparation (Millipore Corp., 18 MΩ). The pH values of solutions were adjusted with sulphuric acid and sodium hydroxide solutions and closely monitored during experiment.

2.2. Preparation of the nanoporous TiO_2 electrode

The TiO_2 sols were prepared by the hydrolysis of titanium butoxide according to the method of Nazeeruddin et al. [2], which yielded a colloid with 45 g/l solid content. Conducting glass (8 Ω/cm, Institute of Beijing Construction Material) was washed in turn with NaOH solution, water, chromic acid washing solution and ethanol. After the pretreatment the electrodes were dip-coated in the TiO_2 colloid for three times. The coated electrode was then fired in a muffle furnace at 440°C for 30 min in air.

2.3. Apparatus and methods

All experiments were performed at room temperature in a conventional three-electrode mode, by which a saturated calomel electrode (SCE) was used as the reference electrode and a platinum mesh as the counter electrode. Potentials reported here are referred to SCE. For the photoelectrochemical measurement the experiment setup was composed of a voltammograph (cv-27, BAS), an AD converter (Maclab 400, AD Instruments) and a computer (7220/200, Macintosh) for sampling the potential and current signals, and 150 W xenon lamp with focusing lenses (HF-200w-95, Beijing Optical Instruments) for illumination. Light intensity changes were made through changing the relative position of the electrolytic cell to the light source, and the intensity was measured with a UV-irradiance meter (UV-A, Instruments of Beijing Normal University).

3. Results

3.1. Influence of applied potential and methanol concentration

Fig. 1 shows the voltammograms recorded at the porous TiO_2 film electrode in different concentrations of methanol under illumination, and in blank electrolyte both under illumination and in the dark. As shown in the figure, for the blank electrolyte in the dark, no current was observable. Likewise, no current was observable in the presence of methanol in the dark (not shown). Under illumination, the photocurrent increased linearly with the applied potential before levelling off. The point at which current levels off with potential shifted to higher potential as the concentration of methanol was increased. This photocurrent–potential characteristic is similar to that of TiO_2 single crystal electrode [26]. In consideration of the considerable amount of defects and/or surface states existing on the electrode, the photoelectrochemical behaviour of the electrode is quite unusual. This may be caused by its nanoporous/nanoparticle nature.

The saturated photocurrent may imply that photogenerated holes or the concentration of methanol at the interface are not enough to facilitate the interfacial reaction. In other words, under the circumstance, the interfacial reaction is

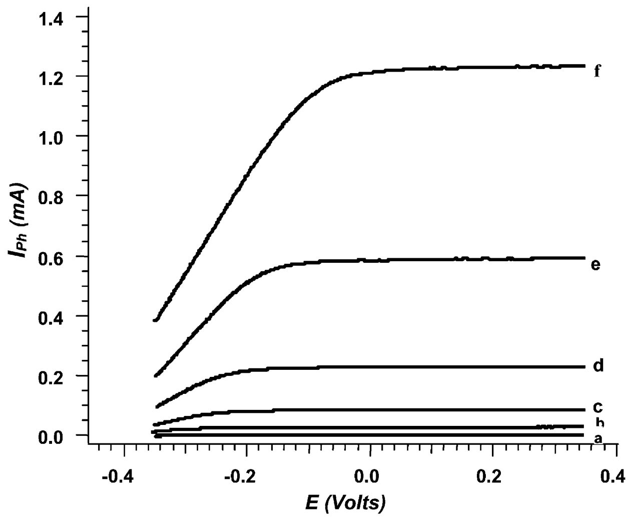

Fig. 1. Voltammograms of the porous TiO_2 film electrode in 0.5 M Na_2SO_4 solution of different methanol concentrations at 6.6 mW/cm^2 light intensity and at scan rate of 10 mV/s: (a) no methanol in the dark; (b) no methanol under illumination; (c) 0.5 mM; (d) 4 mM; (e) 50 mM; (f) 0.75 M.

sluggish in comparison with the migration of photogenerated electrons. To investigate this further, the influence of methanol concentration (C_m from submillimolar to molar level) on the reaction rate was studied. To ensure the migration of photoelectron was not rate-determining step and the interfacial reaction was targeted, the saturated photocurrent was adopted as the indicator of the reaction rate for interfacial charge transfer reaction. Fig. 2 shows the saturated photocurrent (I_{phs}) plotted against the methanol concentration at a given light intensity. As seen from the figure the saturated current increases rapidly in the low concentration domain, then reaches saturation in the high concentration range.

To clarify what causes the photocurrent saturation with respect to methanol concentration here, we processed the data according to Langmuir–Hinshelwood model and plotted $1/I_{phs}$ versus $1/C_m$ of methanol. Fig. 3 shows that reasonable linearity was obtained in the intermediate concentration domain. In the low concentration region the points deviate from the straight line due to the competitive oxidation of water. In the high concentration region the deviation from the straight line was also observed. This is presumably caused by the current doubling effect of the free radical resulting from the reaction of methanol with surface bound hydroxyl radical. When the concentration is high the free radical formed at the valence band may not readily diffuse away from the TiO_2 surface, instead injecting its electron into the conduction band. The kinetics of the photoelectrochemical oxidation of methanol with respect to the methanol concentration agrees well with Langmuir–Hinshelwood model. This suggests that the saturation of saturated photocurrent with respect to methanol concentration be caused by the saturation of methanol adsorption. Given the existence of hydroxyl group on the TiO_2 surface and the nature of methanol, it is most likely that methanol weakly adsorbs on TiO_2 surface via Van der Waals forces. That such high concentration is needed to saturate the saturated photocurrent supports our argument. In the case of strongly adsorbed organic substances (for example, potassium hydrogen phthalate) the concentration needed to saturate the saturated photocurrent is much lower (to be reported elsewhere).

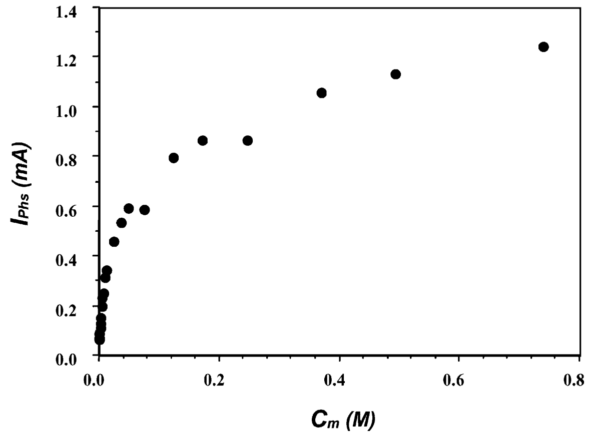

Fig. 2. The dependence of the saturated photocurrent on methanol concentration. Experimental conditions as in Fig. 1.

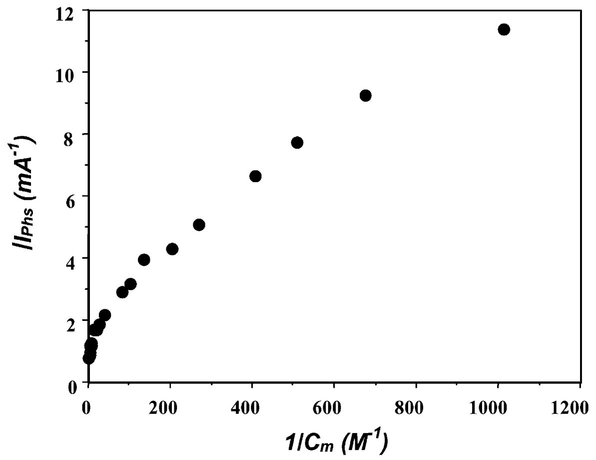

Fig. 3. The plot of the reciprocal saturated photocurrent vs. the reciprocal methanol concentration. Data derived from Fig. 2.

3.2. Dependence of photocurrent on applied potential and light intensity

To further investigate the overall photooxidation process, voltammetry at a given methanol concentration was performed under the incidence of different light intensity. Displayed in Fig. 4 are the voltammograms obtained for a 0.75 M methanol solution. At an each light intensity the photocurrent increases linearly with applied potential, and

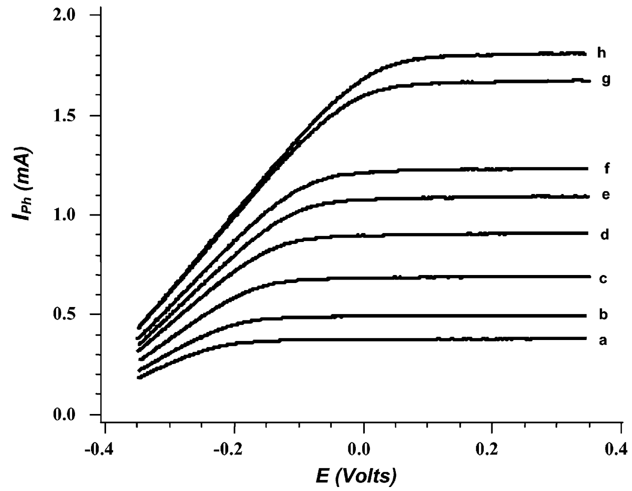

Fig. 4. Voltammograms of the nanoporous TiO_2 film electrode in 0.75 M methanol+0.5 M Na_2SO_4 solution under the incidence of light of different intensities at scan rate of 10 mV/s: (a) 1.68 mW/cm^2; (b) 2.32 mW/cm^2; (c) 3.22 mW/cm^2; (d) 4.35 mW/cm^2; (e) 5.50 mW/cm^2; (f) 6.60 mW/cm^2; (g) 8.41 mW/cm^2; (h) 9.1 mW/cm^2.

then levels off. The linear potential region extends to more positive potentials as the light intensity increases. To study the influence of light intensity on the reaction rate, the saturated photocurrent was taken as the measurable parameter (ensuring that the photogenerated charge separation step did not affect the overall reaction). Plotting the saturated photocurrent against the light intensity gives rise to a straight line shown in Fig. 5(a). It must be pointed out that at any methanol concentration (or even in the absence of methanol), a linear relationship between the saturated photocurrent and light intensity always exists (not shown in the absence of methanol). However, plotting the photocurrent at potentials before the photocurrent levels off against the light intensity gives non-linear curve as shown in Fig. 5(b)–(d). This indicates that in the low potential region the photogenerated charge separation is the rate-limiting step and for different light intensities the efficiency of the photogenerated charge separation is different. The higher the light intensity the higher applied potential is needed for effective charge separation. This explains why in the suspension system at relatively high light intensity the photocatalytic reaction rate no longer changes linearly with light intensity [8]. From the above argument it can been seen that as long as the potential is high enough, the electrons collected (or holes that react with methanol) are proportional to light intensity. This implies that the interfacial reaction with respect to surface bound holes of any form is first order, and most likely this conclusion can be extended to other substances.

3.3. Influence of pH

It is known that the flat band potential and the band edge potential of oxide semiconductors have a Nernstian dependence on the pH of the solutions [17,27]. Hence, changing the pH of solution causes the band edge potential to change. Moreover, the charge status of the oxide depends on the pH of solution. With the TiO_2 suspension system, it has been reported that the reaction rate changes depending on the charging state of reactant in solution, which is attributed to the change of electrostatic interaction between the reactant and the TiO_2 surface [8].

In the present work a series of voltammograms in different pH solutions in the presence and absence of methanol were recorded. From these voltammograms the current onset potentials at different pHs and the saturated photocurrents at different pHs were derived. Fig. 6 shows the dependence of onset potential on the pH and the rest potential on the pH. It should be pointed out that the presence of methanol

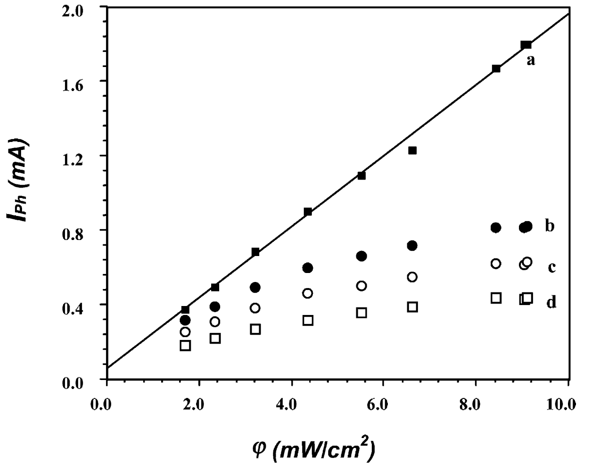

Fig. 5. The plots of photocurrent against light intensity. Data derived from Fig. 4: (a) saturated photocurrent vs. light intensity (■); ((b)–(d)) photocurrent vs. light intensity at (●) −0.20 V, (○) −0.25 V and (□) −0.30 V.

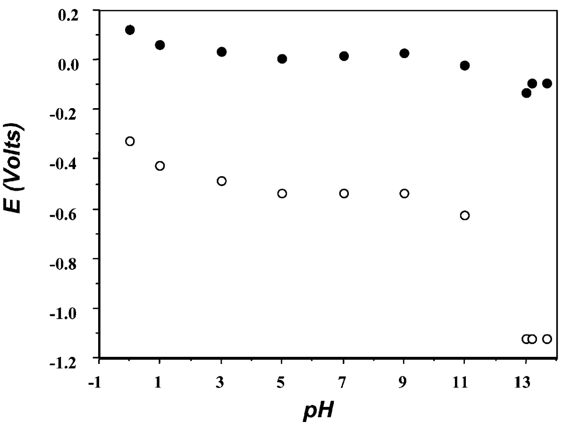

Fig. 6. Photocurrent onset potentials (○) in solutions of different pH values with or without methanol under illumination. Open circuit potential of the electrode (●) in solutions of different pH values with or without methanol in the dark.

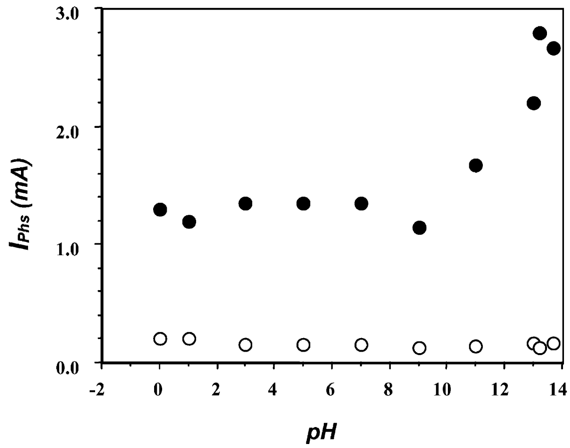

Fig. 7. The saturated photocurrent of the nanoporous TiO_2 electrode in solutions of different pH values with 0.04 M methanol (●) and without methanol (○).

does not affect these two parameters, which indicates the onset potential is an inherent property of the electrode. As seen from Fig. 6 the onset potential is pH dependent at high and low pH values, while in the intermediate pH region the onset potential shows no apparent variation with pH. A similar phenomenon has been reported by Nelson et al. [27]. Interestingly, the rest potential in the presence and absence of methanol exhibits the same trends. Although the open circuit potential is a mixed potential of all the redox potentials in solution, at the surface and at the interface, its trend no doubt partly reflects the change of the electrode surface. Normally the onset potential is approximately equal to the conduction band edge potential and the flat band potential. What causes the deviation of onset potential from the Nernstian dependence on pH is explained in Section 4.

Fig. 7 shows the saturated photocurrent at different pHs in the presence and absence of methanol. In the absence of methanol the saturated photocurrents were small and showed no obvious change over the entire pH range. In the presence of methanol the saturated photocurrents were greatly increased and showed no obvious variation in the pH range 0–9. Considering that methanol molecule is neutrally charged molecule the result is reasonable. However, when the pH exceeded about 9 the saturated photocurrent increased rapidly with pH. This is a very unique response for a neutrally charged molecule.

To find out the role of hydroxide ion in the increase of photocurrent or photooxidation rate, a series of voltammetric experiments were carried out at given methanol concentration in hydroxide ion solutions of different concentrations. Shown in Fig. 8(a) is the plot of saturated photocurrent versus OH^- concentration. A gradually saturated dependence of photocurrent on OH^- concentration was observed. By processing the data according to the Langmuir–Hinshelwood kinetic model, $1/I_{phs}$ versus $1/[OH^-]$ gives a straight line shown in Fig. 8(b). Obviously the hydroxide ion itself is not responsible for the sudden rise in the photooxidation rate.

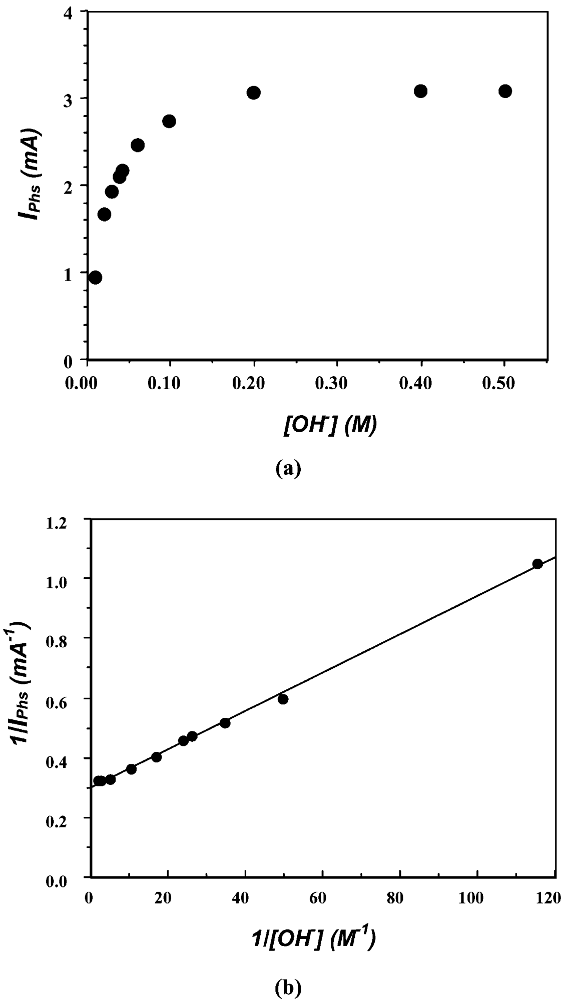

Fig. 8. (a) The dependence of the saturated photocurrent on hydroxide ion concentration in 0.04 M methanol + x M NaOH + $(0.5 - x)$ M Na_2SO_4. (b) The plot of reciprocal saturated photocurrent vs. the reciprocal concentration of hydroxide ion. Data derived from part (a).

4. Discussion

The primary goal of the present study was to investigate the influence of various parameters on the macro-kinetics of photoelectrochemical oxidation to elucidate aspects of the entire photoelectrochemical process. For this reaction system, there are three interfaces as well as the TiO_2 film. They are the SnO_2/TiO_2 interface in series with the TiO_2/electrolyte interface and the TiO_2 film, and together in parallel with SnO_2/electrolyte interface. Each of them plays an important role in the overall charge transfer process. A photocurrent flows only when the photogenerated charge carriers are transferred across the first two interfaces, where the first interface primarily involves electron migration across the film in the electric field, the second one involves the reaction of photogenerated holes or trapped holes with the electron donor (i.e. methanol). One of the special features of the SnO_2 substrate is that itself is a semiconductor and its conduction band is slightly lower than that of TiO_2, and above all it is a good polarisable electrode in aqueous solution, as is demonstrated in Fig. 1. This makes photoelectrochemical reaction occur efficiently and the overall process simpler. In the case of a non-polarisable substrate not only would the photocatalytic reaction be less efficient but also the photoresponse of the system would be more complicated. This situation has been observed by Shiga et al. using gold and platinum as substrates [28].

Because the thickness of the TiO_2 film is smaller than the space charge layer, unlike conventional semiconductor electrodes the thickness of "space charge region" or charge separation layer does not change with applied potential. As a result, the electric field across the film is almost uniform and the electric field is proportional to the potential difference across the film. As long as the speed of the charge transfer reaction at the TiO_2/electrolyte interface and the speed of hole generation can keep up with the speed of electron migration in the electric field, the current should be directly proportional to the applied potential. This argument is supported by our experimental results, as is shown in Figs. 1 and 4, where the potential range of the I_{phs}/E linearity increased as both the concentration of methanol and the light density were increased. Under this circumstance the charge separation or electron migration was the rate-determining step. Whenever either of them cannot keep pace with the increasing speed of electron migration or charge separation under the increasing electric field, saturation of the photocurrent with respect to potential occurs.

When the potential is high enough to ensure that the migration of photoelectrons or charge separation is not the rate-limiting step, the increase in applied potential mainly drops at the TiO_2/solution interface. But unlike the normal electrode reaction where the potential drop can alter the interfacial reaction rate by changing the activation energy, photoelectrochemical oxidation reactions are radical reactions of very low activation energy. Hence, the potential drop at this interface does not alter the interfacial rate of reaction. As a result, the photocurrent reaches saturation with potential and stays constant. Provided that the applied potential is high enough for effective charge separation, the concentration of surface bound hydroxyl radicals is proportional to the light intensity. It is commonly accepted that reaction at the interface is a bimolecular reaction, i.e. surface bound hydroxyl radicals react with methanol molecules [8]. In this situation both the light intensity and methanol surface coverage control the overall photoelectrochemical oxidation process. As a consequence the saturated photocurrent is directly proportional to both light intensity and surface coverage.

The abrupt increase of photocurrent in alkaline solution and the agreement with Langmuir–Hinshelwood rate law with respect to OH^- implies that either the adsorption of hydroxide ion or the participation of hydroxide ion in the pre- or post-oxidation step of methanol brings about the change. A convenient explanation would be that another type of hydroxide ion adsorption site was made available to hydroxide ion in solution. With the OH^- concentration increasing the adsorption of OH^- would reach saturation. As the oxidation reaction occurs via the surface bound hydroxyl group, the rate of reaction would increase and level off with respect to the OH^- concentration in solution. This explanation is ruled out by the observation that in the absence of methanol, in the corresponding pH domain, the photocurrent remains unchanged. This suggests that the amount of surface bound hydroxyl group may be not the determining factor in the overall process. This is reasonable, since the surface bound hydroxyl radical is highly reactive, it hardly accumulates to any considerable extent and the surface bound hydroxyl group concentration at any pH is sufficient to facilitate the relay of photogenerated holes. The linear relationship between the saturated photocurrent and light intensity indirectly supports this argument. Moreover, if the hydroxyl group surface coverage is a determining factor, then the reaction rate should be proportional to total coverage of hydroxyl group, not to the coverage caused by the addition of hydroxide ion in solution.

It has been reported that there are two kinds of adsorbed hydroxyl groups on TiO_2 surface, one is acidic and the other is basic [29]. The basic groups in acidic or slightly basic solutions can be exchanged by any kind of anion, so this kind of site is a positive charged site, as a result it is unlikely to serve as the trap of the photogenerated holes. Whereas the other kind under such pH is in hydroxyl form, so it is more likely only this kind of hydroxyl groups serve as the trap for photogenerated hole. In strong basic solutions, the acidic hydroxyl group on the surface reacts with hydroxide ion and leaves a basic group with negative charge. It adsorbs methanol more strongly, for the hydroxyl groups in alcohol molecules tend to accept electrons from the electron donor via hydrogen bonding.

Consequently there must be a surface reaction:

$$>\!OH + OH^- \rightarrow >\!O^- + H_2O \qquad (1)$$

In equilibrium

$$[>\!O^-] = K[OH^-][>\!OH] \qquad (2)$$

where $>\!OH$ represents the surface bound hydroxyl group, $>\!O^-$ the product of its reaction with hydroxide ion and K is the equilibrium constant. The $>\!O^-$ site may adsorb methanol much faster and stronger than $>\!OH$, consequently the $>\!O^-$ site coverage equals methanol coverage. At a given methanol concentration,

$$\theta_{>O^-} = \theta_m = \frac{[>\!O^-]}{[>\!O^-] + [>\!OH]} \qquad (3)$$

where $\theta_{>O^-}$ represents the surface coverage by $>\!O^-$ and θ_m is the surface coverage by methanol. Substituting Eq. (2) into Eq. (3) gives

$$\theta_{>O^-} = \theta_m = \frac{K[OH^-]}{K[OH^-] + 1} \qquad (4)$$

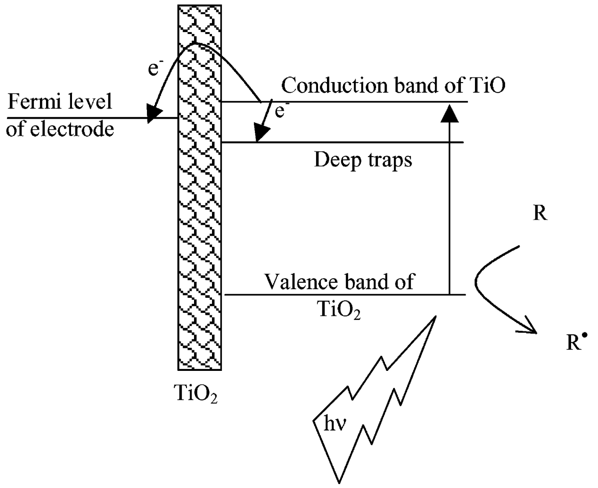

Fig. 9. The schematic diagram of the charge transfer processes at nanoporous TiO_2 electrode.

Hence, at a given methanol concentration the methanol surface coverage is controlled by $[OH^-]$ in solution, which follows the Langmuir adsorption model. As a result, the photocurrent or reaction rate with respect to $[OH^-]$ exhibits a Langmuir–Hinshelwood kinetic behaviour.

It has long been known that semiconductors (especially polycrystalline semiconductor) have structural defects and surface states. For nanoporous TiO_2 film the structural defects and surface states should exist in considerable amount. Based on semiconductor energy band theory we propose a simple model to explain the deviation of onset potential from the Nernstian dependence on pH. The schematic diagram of the model is shown in Fig. 9. As the TiO_2 absorb UV-light, electrons transit to conduction band, and holes are left in the valence band. Once photogenerated electrons and holes are formed they are trapped. Some photogenerated electrons are trapped in deep traps others are trapped by shallow traps. The deep trapping of electrons is thermodynamically favourable. So, unless all the deep traps are filled there would be no shallow trapped electrons, especially when light intensity is relatively low. The difference of onset potential from the flat band potential is most likely caused by the existence of a large amount of deep traps. As illustrated in the schematic, with the presence of electron donor in the solution, if there were no deep electron traps, whenever the electrode potential is higher than the conduction band edge, there would be electron flow. Therefore, the current onset potential would be equal to or very close to the flat band potential. But with the existence of deep traps, if there are free or shallow trapped photoelectrons left after the deep traps are filled, then as the potential increases the free or shallow trapped photoelectrons are drained out. As the electrode potential increases beyond the potential of traps, the deep-trapped photoelectrons start to be drained out. In this case two waves would be expected in the I_{phs}/E curve and, depending on the amount of free photoelectron or shallow trapped photoelectrons, the first wave may be not noticeable. This was observed by Nelson et al. [27]. If there are not enough photoelectrons to fill the deep traps, only one wave is expected. When the pH of the solution increases, the conduction band edge energy goes up, and the onset potential of photocurrent should decrease. Perhaps the potential of photoelectron traps changes with pH differently from the way the band edge potential changes with pH. In low and high pH domains the deep traps uptake the H^+ and OH^- ions more freely, thus its potential change can follow the band edge potential change. In the intermediate pH range the deep traps seem not freely to take H^+ or OH^- ions, thus the difference between the trap potential and the conduction band-edge potential increases as the pH increases. The findings of Hoffmann's group [30] support our idea. In that work, the authors states that there are acidic Ti(IV)OH sites on TiO_2 surface, and the sites trap electron to form Ti(III)OH which is impervious to water. Further evidence is given by Wang et al. [31] who reported that trap density of TiO_2 film was strongly dependent on pH.

5. Conclusion

The immobilisation of the TiO_2 nanoparticles onto conducting glass has allowed for the application of the photoelectrochemical technique to investigate the influence of applied potential bias, light intensity and methanol concentration on the photocatalytic reaction. From the experimental data and the above argument, the rate-limiting step of the overall process varies depending on these factors. At a given light intensity and a given methanol concentration, in low potential region the photooxidation rate increases linearly with potential, so at this stage the migration of photoelectrons across the TiO_2 film or photogenerated charge separation is the rate-limiting step. As the potential bias increases, the interfacial reaction cannot keep pace with the electron migration, at this stage the rate-limiting step is the interfacial charge transfer step. In this case the photooxidation rate changes linearly with light intensity and methanol surface coverage. The interesting I_{phs}/E characteristic at different light intensity and/or methanol concentration is similar to that of the single crystal semiconductor electrode, which is quite unusual for the polycrystalline semiconductor electrode. The unusual onset potential dependence on pH was observed and explained based on the existence of deep electron traps. The abrupt increase of photocurrent in alkaline solution was observed and was explained by the existence of acidic surface bound hydroxyl groups, stronger adsorption to methanol after their reaction with the hydroxide ion and the higher reactivity of the subsequently adsorbed methanol.

Acknowledgements

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