

## Photostability Study of Nanoporous TiO<sub>2</sub> Film Electrodes in Basic Solutions

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**Abstract:** The nanoporous TiO<sub>2</sub> film electrodes have been prepared by a sol-gel deposition process. The photostability of the electrodes in basic solutions has been studied. The results show that the photostability of the electrodes decreases rapidly in strong basic solutions with or without methanol. The reaction of holes to O<sup>2</sup><sub>ad</sub> produces active O<sub>ad</sub> atoms and the products O<sub>ad</sub> atoms oxidize Ti<sup>3+</sup> to Ti<sup>4+</sup> on TiO<sub>2</sub> film surface and subsurface. This results in the TiO<sub>2</sub> film electrodes unstable in basic solutions both without methanol and with too low concentration.

**Keywords:** Photostability, TiO<sub>2</sub> film, photoelectrochemistry.

Semiconducting TiO<sub>2</sub> film is attractive for both solar devices and wastewater treatment. A crucial advantage of using TiO<sub>2</sub> film immobilized over an electrically conducting substrates is that, by applying a bias potential it can accelerate the separation of photogenerated electrons and holes, thereby improving the quantum yield<sup>1-2</sup>. In view of these potential advantages, a large amount of basic theoretical research on the photocatalytic oxidation mechanisms of pollutants has been published<sup>3-4</sup>. However, in acidic solutions, due to photocorrosion, the photostability of TiO<sub>2</sub> film electrodes decreases gradually after a long-time use<sup>5</sup>. In practical studies, we have also noticed that the photostability of TiO<sub>2</sub> film electrodes decreases gradually in basic solution after a short-time use. So far, no detailed study has been reported for this phenomenon during the oxidation of organics in basic solutions.

In this paper, we used the nanoporous TiO<sub>2</sub> film immobilized on conductive glass as study electrodes, methanol, a well-known radical scavenger and a non-specific adsorbent to TiO<sub>2</sub> as the electron donor to investigate the photostability behavior of nanoporous TiO<sub>2</sub> film electrodes in basic solutions.

### Experimental

Titanium butoxide (97%) and methanol (99.8%) were obtained from Shanghai Third Chemical Reagent Co. All other chemicals were analytical reagents and used without further purification. Deionised water(R~18MΩ) was used for all experiments. The

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TiO<sub>2</sub> film electrode was prepared by a sol-gel technique similarly to the procedure described in Ref.6. The area of electrode was 0.5 cm<sup>2</sup>. Electrochemical measurements were carried out in a standard three-electrode system at ~25°C. The TiO<sub>2</sub> electrodes were used as working electrodes, a saturated calomel electrode (SCE) and platinum wire as the reference and counter electrodes, respectively. Photostability was evaluated by the change of photocurrent at 0V (*vs.* SCE). A Potentiostat / Galvanostat Model 273 (Princeton Applied Research) was used in photoelectrochemical measurements. The source of excitation was a 250W xenon lamp (Müller Elektronik Optik, Germany). The TiO<sub>2</sub> film compositions were analyzed by EDAX (X-ray Electron Dispersion Analysis, Model: Phoenix. EDAX, US). The pH of solution was adjusted by adding a small amount of H<sub>2</sub>SO<sub>4</sub> or NaOH. In order to keep the pH of solution and methanol concentration unchanged, solutions were replaced per 10 min during measurements. The electrolyte of 0.5mol/L Na<sub>2</sub>SO<sub>4</sub> was saturated by N<sub>2</sub>.

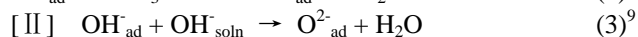
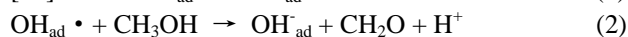
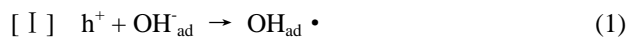
## Results and Discussion

**Figure 1** shows the change of the oxidation photocurrent of methanol at different nanoporous TiO<sub>2</sub> film electrodes in different pH solutions with 0.1 mol/L methanol. As shown in the **Figure**, the oxidation photocurrent of methanol increases with increasing pH of solution, but at the high pH the steady-state photocurrent maintains for a short time. This indicates that the TiO<sub>2</sub> film electrodes are less photostable at high pH than at low pH, though there is higher short-lived photocurrent in the former. In acidic solution, for example at pH 3.20, the decay of the photocurrent was not observed during the experiments, this might be related with the structure of electrodes and pH of solution.

To clarify what causes the decrease of the photostability of TiO<sub>2</sub> film, the influence of methanol concentration was studied at pH 3.20 and pH 12.86, respectively. At pH 3.20, the photocurrent increases with increasing methanol concentration (not show), and all photocurrents are quite stable as curve (a) shown in **Figure 1**. At pH 12.86, the photocurrent also increases with increasing methanol concentration. However, as shown in **Figure 2**, the photocurrent decreases rapidly at low methanol concentration but slowly at high one. These results at least indicate that methanol has no negative effect on the photostability of TiO<sub>2</sub> film electrodes, and it may be related to the pH of solution.

Previous studies have indicated that hydronium and hydroxide ions are potential-determining ions on TiO<sub>2</sub> surface in water<sup>7-8</sup>, because their adsorption changes the surface potential of TiO<sub>2</sub>. This suggests that the adsorption to hydronium or hydroxide ions varies the potential drop in Helmholtz layer, affecting the surface potential of TiO<sub>2</sub> film; consequently, this might result in photocurrent increase with increasing pH.

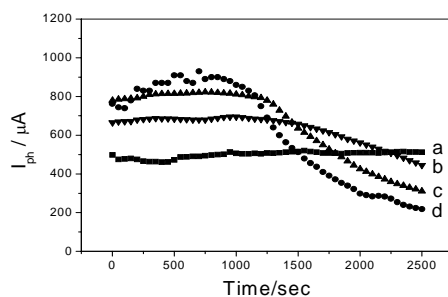
Now let us consider the photostability of the electrodes. In basic solution with methanol, photoformed holes are consumed through the process I and process II<sup>9-10</sup>.



Where subscript ad and soln represent species of adsorbed and solution, respectively. If the resulting  $O_{ad}^-$  atoms from process II are not completely consumed by methanol, they might occupy gradually the oxygen vacancies of TiO<sub>2</sub> film on surface/subsurface and oxidize  $Ti^{3+}$  to  $Ti^{4+}$ , which means the density of oxygen vacancies who act as a role of electron donors under illumination, decreases. While the photocatalytic activity increases with the density of oxygen vacancies<sup>11</sup>. Process I has no effect on the photostability of TiO<sub>2</sub> film. So, the more  $O_{ad}^-$  atoms are, the worse the photostability of TiO<sub>2</sub> film is. In acid solution with methanol, process II can hardly occur due to the lack of OH<sup>-</sup> ions, thus the concentration of  $O_{ad}^-$  atoms produced is negligible and the photostability of the electrodes is high as suggested in curve (a) of **Figure 1**. In strong basic solution with high enough methanol concentration, the resulting  $O_{ad}^-$  atoms are predominantly consumed by methanol and the reaction of oxidizing  $Ti^{3+}$  to  $Ti^{4+}$  by  $O_{ad}^-$  atoms is greatly retarded, so the electrodes is photostable as indicated in **Figure 2**. So the reaction in process II produces active  $O_{ad}^-$  atoms and the products  $O_{ad}^-$  atoms oxidize  $Ti^{3+}$  to  $Ti^{4+}$  on TiO<sub>2</sub> film surface and subsurface. This results in the TiO<sub>2</sub> film electrodes unstable in basic solutions.

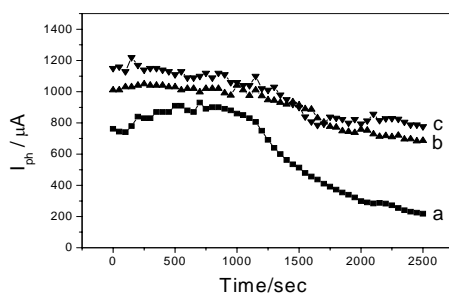
The TiO<sub>2</sub> film compositions, before and after the decrease in photostability, for the same electrode area have been determined by EDAX. As shown in **Figure 3**, the increase of O peak is detected. This result further suggests that the reaction of oxidizing  $Ti^{3+}$  to  $Ti^{4+}$  by  $O_{ad}^-$  atoms results in the TiO<sub>2</sub> films unstable in basic solutions.

**Figure 1** The photocurrent variation with time at different pH values with 0.1 mol/L methanol



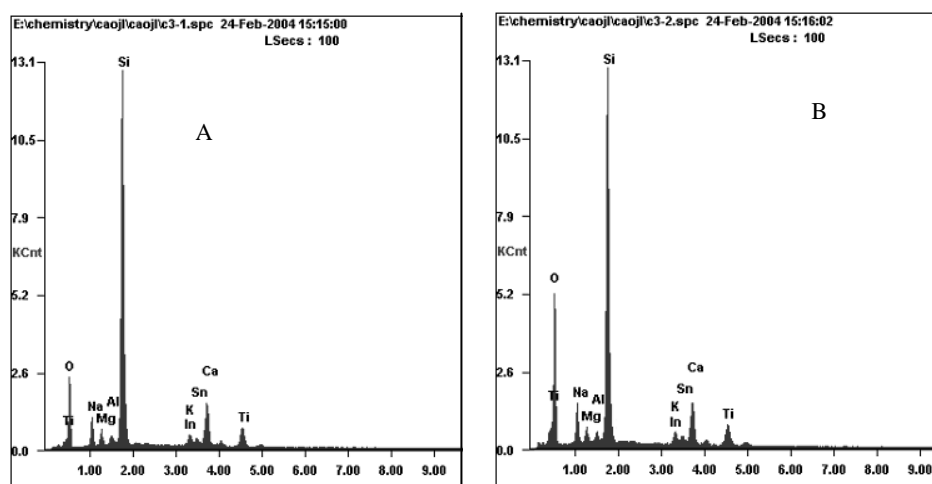
(a) pH 3.20 (b) pH 9.47 (c) pH 10.66 (d) pH 12.86

**Figure 2** The photocurrent variation with time at different methanol concentrations



pH=12.86; (a) 0.1 mol/L, (b) 0.4 mol/L, (c) 0.8 mol/L

**Figure 3** The EDAX spectrum of nanoporous TiO<sub>2</sub> thin film electrode (A) before and (B) after the decrease in photostability



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