

# Photodegradation and Mineralization of Acetic Acid by Titanium Dioxide Films

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**Abstract.** ITO (indium-tin oxide) conductive glass plates were used as a support of Titanium dioxide films. TiO<sub>2</sub>/ITO films were prepared by sol-gel and dip-coating method with cheap inorganic salt TiCl<sub>4</sub> as a precursor. The photocatalytic activity was evaluated by the photocatalytic decomposition of acetic acid in aqueous solution. Results showed that the photocatalytic activity of TiO<sub>2</sub>/ITO films was 20% higher than that of TiO<sub>2</sub> nanopowders for the degradation of acetic acid. The removal rate of acetic acid (25 mg/L) was about 80% after 6h irradiation, while TiO<sub>2</sub>/ITO film calcined at 500°C for 1h with 4-coating times was used as photocatalyst. Furthermore, 74% of the total organic carbon was eliminated after 6h irradiation. It was founded that when the initial concentration of acetic acid was smaller than 40mg/L, the photodegradation of acetic acid accorded with first-order kinetic pattern.

## Introduction

In recent years, environmental pollution has attracted considerable attention of many researchers. Undoubtedly, disposal of organic contaminants in the aqueous solution is the most important in the control of environmental pollution. Titanium dioxide has wide foreground in environmental applications [1][2] for its strong oxidizing powder, nontoxicity and long-term photostability. However, it is not easy to reclaim and reutilize TiO<sub>2</sub> nanoparticles, which limited its application. Researchers immobilized TiO<sub>2</sub> on appropriate support [3][4] in order to reutilize it. In this study, we chose ITO (indium-tin oxide) conductive glass plates as a support of TiO<sub>2</sub> films because its conductive property impeded charge-carrier recombination. Other researchers have also proved the advantages of ITO as substrate [5][6]. Acetic acid is the main contaminant in the furfural waste water, which counts to 1.0-2.5% [7]. While acetic acid is one of the biodegradable organic matter and it is also the final product of most chemical oxidation[8][9], whose removal rate has a direct impact on the mineralization effect of the parent compound. To our knowledge, the study regarding photocatalytic degradation of acetic acid is very limited. In this study, TiO<sub>2</sub>/ITO films prepared by sol-gel and dip-coating method were used in the process of photodegradation and mineralization for acetic acid. Influencing factors of degradation were explored and based on the optimization of process parameters the dynamic mechanism of acetic acid degradation and its mineralization extent were further analyzed. Results of this study should provide a theoretical basis for the photocatalytic oxidation of refractory organic pollutants. And it would be useful attempt to apply TiO<sub>2</sub>/ITO films technology to the actual water treatment.

## Experimental Section

**Preparation of TiO<sub>2</sub>/ITO Films.** All the reagents were of analytical grade and were used without further purification. 2ml of Titanium tetrachloride was added slowly to 500ml of the cold (0°C) ultrapure water (16M Ω • cm) with acutely continuous stirring. After being dialysed, TiO<sub>2</sub> water sol was evaporated under agitation in 60°C water bath until the volume decreased to 80 mL. Steady transparent TiO<sub>2</sub> gel was obtained after aggregating for several days. If water in the TiO<sub>2</sub> water sol was completely evaporated, TiO<sub>2</sub> powder photocatalyst was obtained after calcination. The cleaned ITO conductive glass plates (75mm ×40mm×2mm) were dipped in the TiO<sub>2</sub> gel and withdrawn at a

rate of 10mm/s. After each immersion, the films were dried in the infrared ainer. By repeating the above procedure, TiO<sub>2</sub>/ITO films with different dip-coating times were obtained. There were interference stripes and metalline luster on its surface. After further heat treatment TiO<sub>2</sub>/ITO films used in photocatalytic reaction were obtained. However, calcinations above 550°C was not attempted since the ITO glass was distorted upon that temperature.

**Photodegradation Experiments.** 500mL of acetic acid solution ((its initial concentration was 25mg/L) was added into self-made quartz reactor while TiO<sub>2</sub>/ITO film was fixed on the side of the reactor. The geometric area of the film inserted into solution was typically about 2.8cm<sup>2</sup>. The solution was magnetically stirred, while the air was bubbled to the bottom of the reactor, whose flow rate was 0.8L/min. 400W high pressure mercury lamp (GYZ400, Foshan Electrical and Lighting Co., Ltd.) was installed on the side of reactor, which was 10cm away from the center of the reactor. After the light was turned on, some reaction solution was withdrawn from the reactor at given time intervals and filtered by the membrane of 0.22 μ m for analyses of acetic acid(Waters Breeze HPLC System, American Waters Co.) [10] and total organic carbon levels(Model TOC-V<sub>CPH</sub>, Japan Shimadzu Co.).

## Results and Discussion

**Effect of Heat Treatment on Photodegration.** Fig.1 and Fig.2 show respectively the effect of temperature and time of heat treatment for TiO<sub>2</sub>/ITO film coated four times on the photodegradation of acetic acid. As can be seen from Fig.1, When treated temperature was increased from 100°C to 500°C, the activity of TiO<sub>2</sub>/ITO film also rose. The activity was highest at about 500°C, where TiO<sub>2</sub> film exhibited crystallization of anatase structure, but it began to decrease above 500°C. This result possibly had relations to the crystal structure of TiO<sub>2</sub>/ITO film surface at the different treated temperature [11]. According to Fig.2, the activity of TiO<sub>2</sub>/ITO film was lower for 0.5h while degration rate was 26.5%, which went to the climax as heating for 1h while degration rate was 58.7%. However, the activity droppeded with lengthening calcination time. On the basis of the above results, we adopted TiO<sub>2</sub>/ITO film treated at 500°C for 1h as photocatalyst in the following experiments.



Fig. 1 Degradation rate of acetic acid on samples treated at different temperature for 1h



Fig. 2 Degradation rate of acetic acid on samples treated at 500°C for different

**Effect of Initial Concentration of Acetic Acid.** The effect of initial acetic acid concentration on photodegradation efficiency is shown in Fig.3. It is observed that the photodegradation conversion of acetic acid decreased with an increase in the initial acetic acid concentration. The initial photocatalytic rates(  $r_0$  ) were obtained according to Langmuir-Hinshelwood kinetics equation (Abbreviated to L-H model) and the initial acetic acid concentration( $c_0$ ). The relationship between initial photocatalytic reaction rates(  $r_0$  ) and initial acetic acid concentration ( $c_0$ ) was illustrated in Fig.4. when  $c_0 \leq 40$ mg/L, the reactant molecules on the surface of TiO<sub>2</sub>/ITO film did not attain saturated absorption, reaction rate was mainly determined by the reactant concentration so that  $r_0$  swiftly increased with increasing  $c_0$ , the photocatalytic reaction of acetic acid is a first-order reaction. When  $c_0 \geq 40$  mg/L,  $r_0$  increased slowly with the increase of  $c_0$ , the absorption of the reactant molecules on the surface of TiO<sub>2</sub>/ITO film gradually reached saturation. Therefore the reaction rate

completely depends on the amount of electrons and holes, it has nothing to do with the reactant initial concentration. The photodegradation of acetic acid accorded with zero-order kinetic pattern. The above results exactly coincided with L-H model.

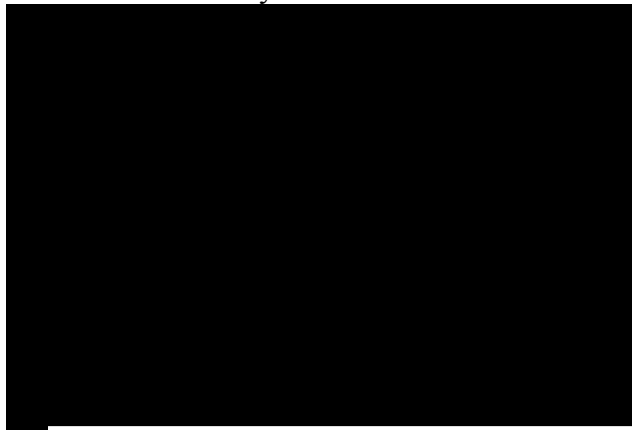


Fig. 3 Effect of initial acetic acid concentration on photodegradation rate

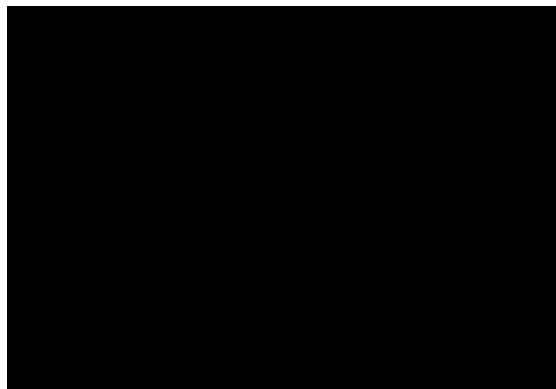


Fig. 4 Relationship between solution initial concentration and initial rate

**Degradation Efficiency of TiO<sub>2</sub>/ITO Films with Different Dip-coating Times.** The effect of dip-coating times on the degradation of acetic acid was illustrated in Fig.5. When the coating times from 1 to 4, quantity of TiO<sub>2</sub> involved in the photodegradation reaction on the film surface increased gradually, and photocatalytic activity enhanced also. The photocatalytic activity of TiO<sub>2</sub>/ITO film reached the highest value with 4-coating times. However, with increasing the coating times, the multi-layered films undergone a relatively long calcination time and contained larger TiO<sub>2</sub> particles[11], which led to efficient surface area in relation to photocatalytic reaction decreases, and then the photocatalytic activity weakened. It was also founded in Fig.5 that the photoactivity of TiO<sub>2</sub>/ITO film was 20% higher than that of TiO<sub>2</sub> powder. Because ITO conductive glass had the favorable electric property and good transmittance to the visible light, on whose surface there was a layer of SnO<sub>2</sub> film immersed Indium. Therefore, as substrate of TiO<sub>2</sub>/ITO film, ITO not only effectively restrained charge recombination of the photogenerated electron/hole pairs but also accelerated formation of more hydroxyl radicals that have powerful oxidation function [12].

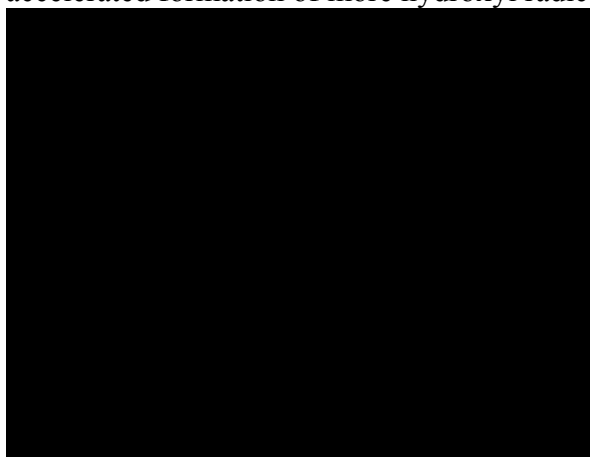


Fig. 5 Effect of dip-coating times on the degradation of acetic acid

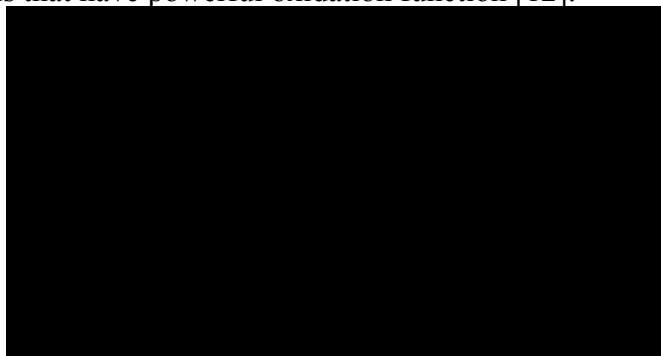


Fig. 6 Change of residual rate of TOC or Acetic Acid  
 (a) variation of TOC with ITO present;  
 (b) degradation of acetic acid with ITO present;  
 (c) variation of TOC with TiO<sub>2</sub>/ITO present;  
 (d) degradation of acetic acid with TiO<sub>2</sub>/ITO present.

### TOC Removal in the Photodegradation

photodegradation of acetic acid with TiO<sub>2</sub>/ITO film and ITO is showed in Fig.6. About 48% of acetic acid with initial concentration at 25 mg/L and 75% of the total organic carbon was remanent after 6h irradiation with ITO present. The residual rate of TOC was always more than that of acetic acid. It was suggested that acetic acid was decomposed into some smaller molecule compounds that affected the TOC amount. After TiO<sub>2</sub>/ITO film coated four times was added to the reaction, about 20% of acetic acid and 26% of the total organic carbon was remanent after 6h irradiation. The residual rate of TOC is a little more than that of acetic acid. Yet they synchronously decreased with increasing

illumination time. The reason may be that acetic acid and byproducts in the photodegradation were photodegraded at same time by TiO<sub>2</sub>/ITO film.

## Conclusion

Photocatalytic degradation of acetic acid was accomplished with TiO<sub>2</sub>/ITO films, which were prepared by sol-gel and dip-coating method with cheap inorganic salt TiCl<sub>4</sub> as a precursor. Effect of various parameters such as heat-treated temperature and time, coating layers of TiO<sub>2</sub> film and the initial concentration of solution on the activity were investigated to study the optimal photocatalytic condition of acetic acid. According to the results, the photocatalytic activity of TiO<sub>2</sub>/ITO films was 20% higher than that of TiO<sub>2</sub> nanopowders for the degradation of acetic acid. The removal rate of acetic acid (25 mg/L) was about 80% after 6h irradiation, while TiO<sub>2</sub>/ITO film calcined at 500°C for 1h with 4-coating times was used as photocatalyst. Furthermore, 74% of the total organic carbon was eliminated after 6h irradiation. It can be presumed that acetic acid and byproducts in the photodegradation of acetic acid were photodegraded at same time by TiO<sub>2</sub>/ITO film. When the initial concentration of acetic acid was smaller than 40mg/L, the photodegradation of acetic acid accorded with first-order kinetic pattern. This study provided a foundation for TiO<sub>2</sub>/ITO films process to be used in actual water treatment.

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