*Articles*

# A Novel Composite Electrode of Photocatalyst-$TiO_2$/C Loading on the Surface of the Air (Oxygen) Electrode

**WANG, Yu-Ling(王玉玲) CAI, Nai-Cai*(蔡乃才) WANG, Ya-Ping(王亚平)**
**ZHONG, Jia-Sheng(钟家圣)**
*College of Chemistry and Molecular Science, Wuhan University, Wuhan, Hubei 430072, China*

**The methods for preparing the $H_2O_2$ generating air (oxygen) electrode and the composite electrode of photocatalyst-$TiO_2$/C loading on the surface of the air (oxygen) electrode were introduced. In the case of the composite electrode, the current efficiency of electro-generated $H_2O_2$ is higher than 80% ($J \leqslant 15$ mA/cm$^2$). The degradation of aniline was used as an example to measure the influence of the composite electrode and compared with the system in which the air (oxygen) electrode and the photocatalyst-$TiO_2$ were separated. The results confirmed that the composite electrode played an active role on accelerating the degradation rate of aniline. According to the measurement of the polarization curves of composite electrode and $TiO_2$ photo anode, and of the adsorbing amount of aniline on the surface of the composite electrode, the principle of descending the recombination rate of photo-generated electron and hole and of enhancing the oxidation rate of organic molecule was described. The mechanism about the degradation of aniline was also discussed.**

**Keywords** air (oxygen) electrode, photocatalyst-$TiO_2$, degradation, aniline

## Introduction

Recently many laboratories have undertaken the study on degradation of the toxic organic contaminants in the industrial wastewater, such as aniline, chlorophenol, chloroform, *etc*.[1,2] which are bio-refractories in the light of their stable structures. Recently a kind of new method by producing hydroxyl radicals (·OH) to destroy the organic molecule, which is called AOP (advanced oxidation process) has become the research focus of the theory and technology in water-treatment chemistry.[3] ·OH is a strong oxidant [its normal electric potential is 2.80 V, which is little lower than that of F (2.87 V)], so it can destroy many toxic and bio-refractory organic contaminants to $CO_2$, $H_2O$ and inorganic ions, which is called mineralization of organic molecule.[4]

The main ways to generate ·OH include Fenton's reagent oxidation,[5] electrochemical oxidation of the water,[6] photochemical excitation $H_2O_2$ or $O_3$[7] and photocatalytic oxidation.[8] To further improve the mineralization rate of the organic pollutant, the composite electrode on which the $TiO_2$ photocatalyst was directly loaded on the surface of the air (oxygen) electrode was investigated. The more interesting experimental results have been obtained. In this paper, the methods for preparing the air (oxygen) electrode and the composite electrode were described, and the efficiency and principle of the composite electrode in accelerating the mineralization rate of organic molecule were investigated. Meanwhile, aniline was chosen as a model to establish the reaction mechanism of the organic molecule in the composite electrode system.

## Experimental

### *Preparation of air (oxygen) electrode*

The air (oxygen) electrode was made up of waterproof gas diffusion film, catalytic film and conductivity network. Waterproof gas diffusion film consisted of acetylene black and emulsion polytetrafluoroethylene including

* E-mail: nccai@whu.edu.cn
Received June 14, 2001; revised September 20, 2001; accepted November 9, 2001.
Project supported by the National Natural Science Foundation of China (No. 20071026).

*p*-octyl polyethylene glycol phenyl ether (OP) and catalytic film consisted of activated carbon and emulsion polytetrafluoroethylene (including OP). After mixing the raw materials according to a certain mass proportion, the mixture was rolled into the membrane. The thickness of the two films was 1 mm and 0.1 mm respectively. After being extracted the OP from the film with acetone, the gas diffusion film, conductivity network and catalytic film were pressed together using a hydraulic press. Subsequently, the electrode was sintered at 380 ℃ for 30 min.

*Preparation of composite electrode*

10 g of $TiO_2$ powder (anatase, average particle size of 40 nm) was well mixed with absolute alcohol (100 mL). 22 g of fine activated carbon was added and stirred fully. After the absolute alcohol had been dried under infrared light, the mixture of $TiO_2$ and activated carbon were distributed on the catalytic film of the air (oxygen) electrode, on which emulsion polytetrafluoroethylene was previously sprayed. After been pressed, it was sintered at 380 ℃ for 30 min. After sintering, activated carbon still existed and its weight was not found reduced in the experiment. Thus the composite electrode was formed, as shown in Fig. 1.

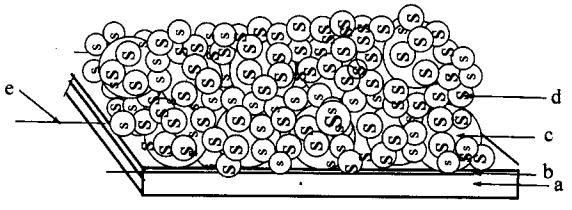


**Fig. 1** Schematic representation of the composition of the composite electrode. a, gas diffusion layer; b, catalytic layer; c, activated carbon; d, $TiO_2$ particle; e, conductivity network.

*Preparation of* $TiO_2$ *catalytic film supported on* Ti

Tetrabutyl titanate [$Ti(OC_4H_9)_4$], HOAc and absolute alcohol were used to prepare the $TiO_2$ sol, which was supported on the pure titanium plate with the dipping method, and after thermal treatment, the $TiO_2$/Ti electrode would be formed (the detailed preparation has been reported in reference[9]).

*Preparation of* $SnO_2$-F/Ti *electrode*

An alcoholic solution of $SnCl_2 \cdot 5H_2O$ (containing 10.0 g of $SnCl_2 \cdot 5H_2O$, 0.1 g of $NH_4F$ and 100 mL of alcohol) was sprayed repeatedly to the titanium substrate, which was previously polished and etched in 10% oxalic acid at 100 ℃ for 2 h to form a crude surface. Then it was calciniced at 600 °C for 1 h in muffle furnace. Finally, a layer of $SnO_2$ film doped F was formed on the titanium substrate.

*Reaction apparatus*

Fig. 2a is the reaction apparatus of the composite electrode system. The reaction cell was made of organic glass ($V$ = 1 L). The composite electrode was adhered to the both sides of the cell as the cathode and the $TiO_2$/C photo-catalytic layer of the electrode was kept in touch with the solution. In the middle of the cell the $SnO_2$-F/Ti electrode as the anode was laid up. The low-pressure mercury lamp was put between the cathode and the anode. During the reacting process, the solution was stirred with a magnetic bar. The reaction was carried out at room temperature for 4 h.

Fig. 2b represents the reaction apparatus in which the air (oxygen) electrode and $TiO_2$/Ti catalytic film were separated.

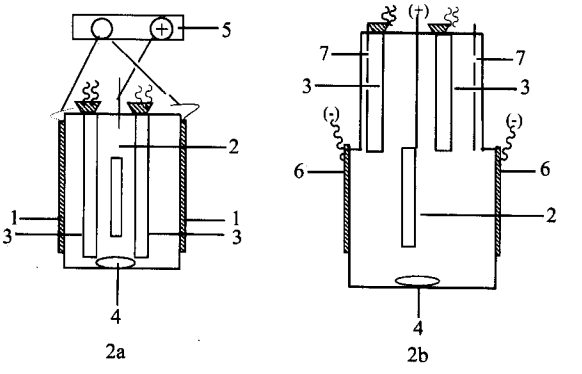


**Fig. 2** Schematic representation of the reaction apparatus. (2a) Type of composite, (2b) type of air (oxygen) electrode and $TiO_2$/Ti catalytic film separated. 1, composite electrode (12 × 8 $cm^2$); 2, $SnO_2$-F/Ti electrode; 3, low pressure mercury lamp (8 W, 254 nm); 4, magnetic bar; 5, D. C. constant current regulator; 6, air (oxygen) electrode (12 × 8 $cm^2$); 7, $TiO_2$/Ti (12 × 8 $cm^2$).

*Measurement of cathode polarization curves of the composite electrode and the photoanode polarization curves of the* $TiO_2$/Ti

The measurement system is shown in Fig. 3, including the electrolysis cell, potentiostau and X-Y recorder. The cathode polarization curve of the composite electrode was measured with the dynamic potential scanning. The voltage scanning speed was 5 mV.

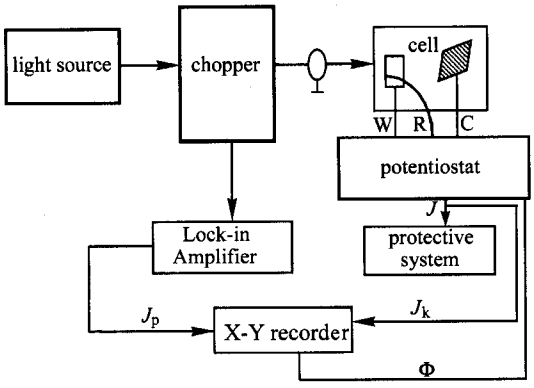


**Fig. 3** Schematic representation of the polarization curves measurement apparatus. W, working electrode; R, reference electrode (SCE); C, counter electrode (Pt); $J_k$, dark current; $J_p$, photo-current; Φ, electode potential.

While measuring the photo-anode polarization curves of the $TiO_2$/Ti photo-catalytic film, the high-pressure mercury lamp was used as the light source (150 W), which was mediated to square wave with the 9479-chopper. The positive scanning was carried on to $TiO_2$/Ti photo catalytic film at 5 mV/s. The photo-current of the film was amplified by 128A Lock-in Amplifier. The curve of potential-photocurrent was recorded by a X-Y recorder.

*Measurement of the efficiency of generating* $H_2O_2$ *on the air (oxygen) electrode and the composite electrode*

The overall concentration ($C_1$) of $H_2O_2$ remaining in solution after electrolysis was determined by titration with potassium permanganate. Assuming that the reduction of $O_2$ as follows: $O_2 + 2H^+ + 2e \rightarrow H_2O_2$, the theoretical value ($C_2$) of concentration of $H_2O_2$ was calculated on basis of the Faradic law. The current efficiency ($\xi$) of generating $H_2O_2$ is $C_1/C_2$.

*Mineralization rate of aniline*

The chemical oxygen demand (COD) refers to the material amount present in the solution that could be oxidized by the strong oxidant (*e. g.* dichromate). In our experiment, the mineralization rate was indicated by the percentage ($\eta$) of the remaining COD in solution ($[COD]_t/[COD]_0$, $[COD]_t$ and $[COD]_0$ are respectively the value when the reaction time is $t$ and before the reaction $[COD]_0 = 2250$ mg/L). The COD of the solution was measured by dichromate method with COD measurement equipment (model HH-5).

*Analysis of the composite electrode morphology*

The morphology of the surface of the composite electrode was observed with SEM (Model JEOL JEM-100XII made in Japan).

## Results

*Morphology of the composite electrode*

It could be seen from Fig. 4 that the $TiO_2$/C layer of the composite electrode has the characteristic of microporosity and high-specific surface area.

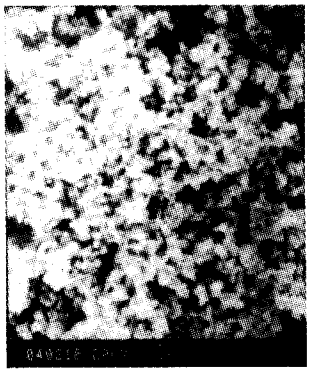

**Fig. 4** SEM top-view of the composite electrode.

*Current efficiency of generating* $H_2O_2$ *on the air (oxygen) electrode and the composite electrode*

From Fig. 5, it can be seen that the air (oxygen) electrode possesses the better electrochemical properties of generating $H_2O_2$. When the $TiO_2$/C photo-catalytic film

was loaded on the surface of the air (oxygen) electrode, the efficiency of generating $H_2O_2$ had a little descendent. However, the efficiency was still higher than 80% at $J \leqslant 15$ mA/cm$^2$.

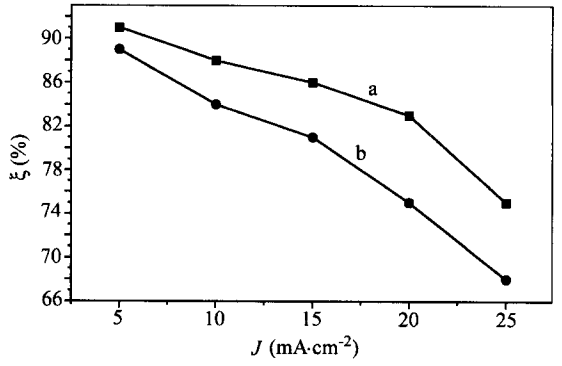


**Fig. 5** Relation of the current efficiency ($\xi$) of generating $H_2O_2$ on air (oxygen) electrode (a) and composite electrode (b) with current density.

*Mineralization rate of aniline in two different kinds of reaction systems*

Comparing to the curves of (a) and (b) in Fig. 6, the mineralization rate of aniline in the composite electrode system (b) is obviously higher than that in the system (a) in which air (oxygen) electrode and the $TiO_2$/Ti photo-catalytic film are separated. When the reaction was carried out for 3 h, the mineralization rate of aniline in composite electrode system was 26% higher than the latter. However, the difference is obviously reduced at $t = 4$ h.

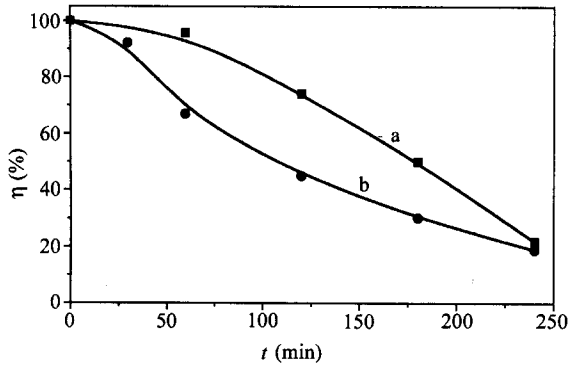


**Fig. 6** Variation of the percentage ($\eta$) of remains of COD in solution with reaction time ($t$) in different system (cathode: $J = 10$ mA/cm$^2$). (a) air (oxygen) electrode and $TiO_2$/Ti separated system, and (b) composite electrode system.

*Cathode polarization curve of the composite electrode and the photo-anode polarization curve of the* $TiO_2$/Ti

From the photo-anode polarization curve (a) of the $TiO_2$/Ti film in Fig. 7, the photo-current onset potential which is often used for evaluating the flatband potential[10] is $-0.4$ V or so. From the cathode polarization curve (b) of the composite electrode, the polarization potential of the composite electrode at 10 mA/cm$^2$ is nearly 0 V (SCE), thus it is possible that the $TiO_2$ photo-catalyst of the compositeelectrode obtains a polarization value more than 0.4 V relative to the flatband potential.

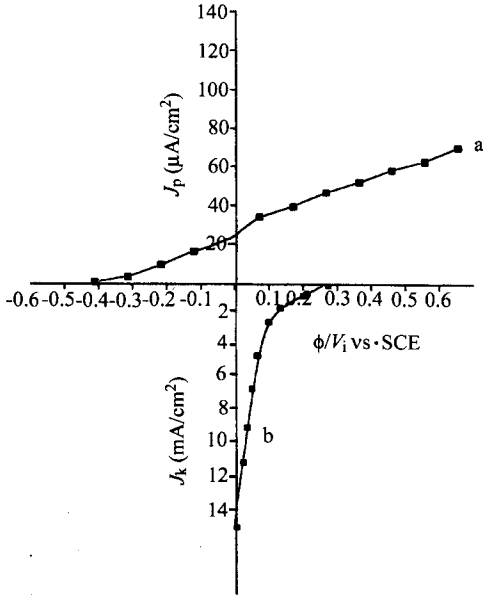


**Fig. 7** Photoanode polarization curve of $TiO_2$/Ti film (a) and cathode polarization curve of the composite electrode (b).

*Adsorption of aniline on the interface between the composite electrode and solution*

The COD of the solution was found descended when the composite electrode was kept in touch with the aniline solution. Amount of saturated adsorption of the aniline ($6.9 \times 10^{-4}$) was obtained according to the measurement result (48 mg/L) of the descendent of COD in the solution when it reached saturated adsorption.

## Discussion

Seen from the structure representation in Fig. 1, $H_2O_2$ that was generated on the surface of catalytic layer

of the air (oxygen) electrode must pass through the $TiO_2$/C photocatalyst layer to enter the bulk solution. The narrow passage of the $TiO_2$/C photo-catalytic layer would influence the transmitting rate of $H_2O_2$ and lead to enhancing of self-decomposition rate of $H_2O_2$ or further reduction of $H_2O_2$ to $H_2O$ in the inner of the composite electrode. This negative influence would be more prominent under the large current density of the air (oxygen) electrode, as represented the descending phenomena of the current efficiency in Fig. 4. In spite of this, it could not influence the mineralization rate of aniline in the composite electrode system. On the contrary, as indicated in Fig. 6, the composite electrode played an active role on accelerating the mineralization rate of aniline.

The reason that the composite electrode plays an active role on the mineralization of aniline lies on the following effects:

(1) The properties of high-specific surface area of $TiO_2$/C layer (as shown in Fig. 4) play an excellent role on adsorbing the organic molecule in the solution, leading organic molecule to accumulation on the interface between the electrode and the solution.

(2) Once the $H_2O_2$ generated on the surface of the catalytic layer of the air (oxygen) electrode diffused out, it would be decomposed by U.V., forming ·OH:[11]

$$H_2O_2 + h\nu \rightarrow 2\cdot OH$$

Then the concentration of ·OH near the surface of the electrode would be higher than that in the bulk solution. So the probability of ·OH reacting with organic molecule (RH) gathered on the surface of the electrode would be increased.

(3) Since $TiO_2$/C photo-catalytic layer was made by immobilizing the $TiO_2$($\phi$ 40 nm) on the high-specific area of activated carbon, it has the benefit of increasing the irradiated surface area and heterogeneous photo-catalytic reaction area of $TiO_2$.

(4) When the surface of the $TiO_2$ was irradiated by U.V., the photo-generated electron ($e^-$) and the photo-generated hole ($h^+$) would be produced. The energy of holes in the valence band of $TiO_2$ is about $-7.5$ eV, so holes react easily with $H_2O$ or organic molecule adsorbed on the surface of $TiO_2$/C photo-catalytic layer:[12]

$$TiO_2(e\text{—}h) + h\nu \longrightarrow TiO_2(e^-, h^+)$$
$$RH + h^+ \longrightarrow R\cdot + H^+ \dashrightarrow CO_2 + H_2O$$
$$H_2O + h^+ \longrightarrow \cdot OH + H^+$$

The reaction process of photo-generated electrons with $O_2$ is as follows:[12]

$$O_2 + e \longrightarrow \cdot O_2^- \longrightarrow HO_2\cdot \longrightarrow H_2O_2 \xrightarrow{h\nu} \cdot OH$$

In the meantime, the photo-generated electron can be recombined by the hole:

$$TiO_2(e^-, h^+) \longrightarrow TiO_2(e\text{—}h)$$

Therefore, it is necessary to descend the recombination rate between photo-generated electron and hole in order to improve the photo-catalytic activity of $TiO_2$. It has been reported that externally applied anodic bias greatly improves the efficiency of charge separation by driving the photo-generated electrons to the cathode.[13] From the results of Fig. 7, it can be inferred that the $TiO_2$ photocatalyst on surface of air (oxygen) electrode at 10 mA/cm$^2$ would obtain a anodic bias more than +0.4 V relative to the flat band potential. Therefore, the $TiO_2$ photocatalyst on the surface of the air (oxygen) electrode would possess much lower photo-generated recombination rate than the separated $TiO_2$/Ti film.

Due to the cooperative action of many active elements above, the degradation dynamic behaviors of aniline on the composite electrode are remarkably faster than those in the separated system (as shown in Fig. 6). Nevertheless, with the duration of time such as 4 h, the difference of the degradation rate of aniline is notably reduced in the two different systems. The reason is that the concentration of the organic molecule becomes very low in the solution and on the surface of the composite electrode at later period of the reaction.

A working principle of the composite electrode and the degradation mechanism of aniline were proposed based on the above mentioned results and discussion (Fig. 8). In the reaction system, organic molecule with ·OH and hole performed a series of reactions. There were various kinds of oxidation reactions from the interface of the composite electrode to the whole solution . However , the

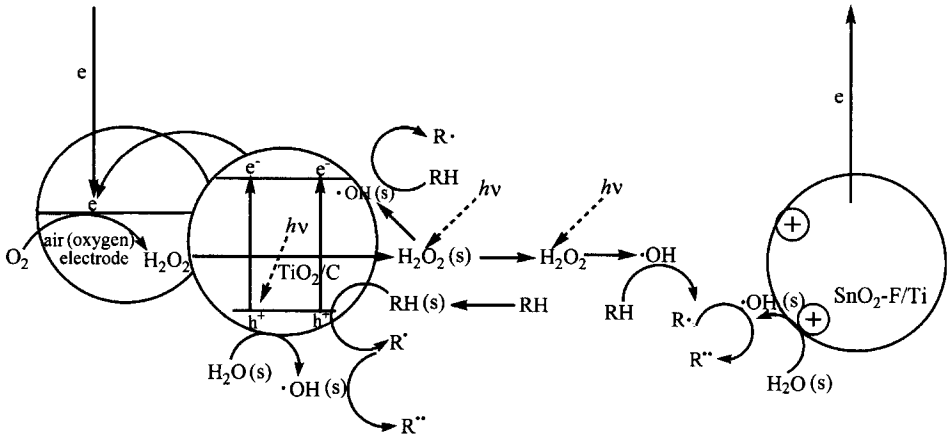


**Fig. 8** Schematic representation of the reaction mechanism in the composite electrode system. RH—organic molar; (s)—adsorbing material; R·, R··—oxidation products of organic molecule.

reactions occurred on the interface of the composite electrode made important contribution to the overall reaction rate.

## Conclusions

The composite electrode not only keeps the higher efficiency to generate $H_2O_2$, providing the material resource to produce the ·OH, but also makes $TiO_2$/C photo-catalyst obtain positive potential (relative to the flat-band potential) provided by air (oxygen) electrode, resulting in descending of the recombination rate between photo-generated electron and hole. In addition, the $TiO_2$/C photo-catalytic layer on the surface of the composite electrode can create an excellent condition to increase the absorbing of the U. V., to enhance the area of photo-catalytic reaction and to adsorb the organic molecule from water because of its properties of micro-porosity and high specific-area. Due to the cooperative action of many active elements, the mineralization rate of aniline in the composite electrode system is higher than the reaction system in which the $TiO_2$/Ti film and the air (oxygen) electrode are separated. Nevertheless, the difference of degradation dynamic behaviors of aniline in the two systems is notably reduced at the later stage of the reaction, for the concentration of organic molecule becomes very low in the solution and on the surface of the electrode.

## References


1 Enrique, B.; Rose, M. B.; Elisobet, L. *J. Electrochem. Soc.* **1995**, *142*, 1733.
2 Enrique, B.; Eva, M. *J. Electrochem. Soc.* **1996**, *143*, L49.
3 Oturan, M. A. *J. Appl. Electrochem.* **2000**, *30*, 475.
4 Polcar, A. M.; Palmas, S.; Renoldi, F.; Masscia, M. *J. Appl. Electrochem.* **1999**, *29*, 147.
5 Richard, G. Z. *Environ. Sci. Technol.* **1992**, *26*, 313.
6 Vitt, J. E.; Johnson, D. C. *J. Electrochem. Soc.* **1992**, *139*, 774.
7 Glaze, H. W.; Kang, J. W. *Ozone: Sci. Eng.* **1987**, *9*, 335.
8 Zoltner, W. A.; Hiu, C. G.; Anderson, J. M. *CHEMTECH* **1993**, *5*, 21.
9 Cai, N.-C.; Huang, X.-J.; Luo, L.-M. *Chin. J. Chem.* **2001**, accepted.
10 Zha, Q.-X. *The Dynamics of Electrode Process*, Science Publishing House, Beijing, **1987**, p. 507 (in Chinese).
11 Wang, Y.; Hong, C.-S. *Water Res.* **1999**, *33*, 203.
12 Kamoto, K.-I.; Yamamoto, Y.; Tanaka, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2015.
13 Dong. H. K.; Marc, A. A. *Environ. Sci. Technol.* **1994**, *28*, 279.


(E0106142 LI, L. T.; LING, J.)