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Photoelectrocatalytic degradation of Rose Bengal

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Abstract: An innovative photoelectrode, TiO_2/Ti mesh electrode, was prepared by galvanostaticanodisation. The morphology and the crystalline texture of the TiO_2 film on mesh electrode were examined by scanning electronic microscopy and Raman spectroscopy respectively. The examination results indicated that the structure and properties of the film depended on anodisation rate, and the anatase was the dominant component under the controlled experimental conditions. Degradation of Rose Bengal(RB) in photocatalytic(PC) and photoelectrocatalytic (PEC) reaction was investigated, the results demonstrated that electric biasing could improve the efficiency of photocatalytic reaction. The measurement results of TOC in photoelectrocatalytic degradation showed that the mineralisation of RB was complete relatively. The comparison between the degradation efficiency of RB in PEC process and that in aqueous TiO_2 dispersion was conducted. The results showed that the apparent first-order rate constant of RB degradation in PEC process was larger than that in aqueous dispersion with 0.1%—0.3% TiO_2 powder, but was smaller than that in aqueous dispersion with 1.0% TiO_2.

Keywords: mesh electrode; anodisation; TiO_2; photoelectrocatalytic oxidation; Rose Bengal

Introduction

Recently twenty years, the photocatalytic oxidation of semiconductor, TiO_2, used for the treatment of water has been paid close attention by many researchers. Many investigations has shown that photocatalytic degradation of TiO_2 provides an effective technological method for the degradation of the organic contaminants in water(Ollis, 1991; 1993; Hidaka, 1992; Ross, 1994; Gao, 2000). In most of the applied cases, TiO_2 aqueous suspensions have been used. However, this method has some shortcomings: the recovery of TiO_2 particles leads to several technological difficulties, and the quantum yield is very low (less than 10% generally; Aurian-Blajeni, 1980; Ma, 1998). The great efforts are made for overcoming above shortcomings. Having TiO_2 particles fixed on a support, even if, can overcome some technological difficulties of the recovery of TiO_2 particles, the specific surface of reaction and the rate of substance transfer is decreased obviously, and the problem of low quantum yield is also not solved. In this study, dyestuffs-one class of typical organic pollutants in industry wastewater were used as objective, an innovative mesh TiO_2 film electrode was used as photoelectrode, by researching the catalytic activities in the process of the photoelectrocatalytic oxidation of Rose Bengal, some experimental basses were provided for accelerating the practical application of TiO_2 photocatalytic oxidation technology in water treatment.

1 Experiment

1.1 Materials

Titanium mesh(purity > 99.6%, nominal aperture 0.19 mm, wire diameter 0.23 mm, wires/inch 60 × 60, open area 20%, twill weave) was purchased from Goodfellow Cambridge Limited. Titanium dioxide powder was purchased from BRH Laboratory Supplies Poole. Rose Bengal (Tetraiodnate 4, 5, 6, 7-tetrachlorofluorescein, RB) was purchased from the Aldrich Chem. Co., and its molecular structure is shown in Fig.1. Other chemicals were of analytical reagent grade and used without further purification. Doubly distilled water was used throughout this study.

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1.2 Experimental installation and equipment

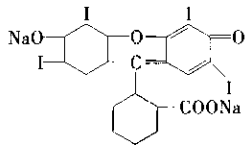

Fig.1 Molecular structure of Rose Bengal

The photoelectrocatalytic reactor system is shown in Fig. 2. The main components were the cylinder quartz cell with the size of 25 mm in diameter and 50 mm in highness, a 20W- ultraviolet light source (NEC T10 BLACKLIGHT), and a potentiostat (ISO-TECH 1PS 1810H). The intensity of light was 2.2 mW/cm^2 at 1.5 cm into position where the TiO_2 electrode was placed. A Pt wire(40 mm in length with a 0.4-mm diameter) and titanium mesh supported TiO_2 film were used as the work-electrode and the counter-electrode respectively. Blak-ray UV meter: UVP Inc, Model No. J 221; scanning electronic microscope(SEM) meter: Leica Stereoscan 400i Series; raman spectroscopy(RS) meter: a laboratory-assembled RS examination system, mainly including Coherent Innva 70 CW argon laser, Spex 1403 monochromator, PMT Hamamatus R943 – 2 photomultiplier tube; UV-visible spectrophotometer: Genesys 2; TOC: SHIMADZU TOC 5000A. Laboratory-assembled HPLC analysis system: including ISCO Model 2350 High Pump, RESTEK Pinnacle Octyl Amine 5 μm 250 × 4.6 mm Column, Water™ 486 Tunable Absorbance Detector.

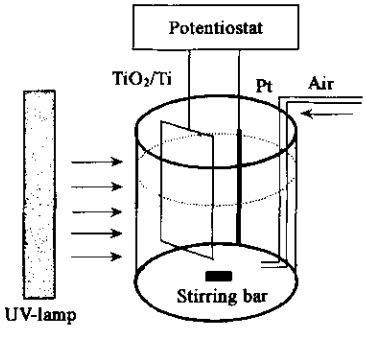

Fig.2 Diagram of reactor for the system of photoelectrocatalytic reaction

1.3 Procedure

1.3.1 Preparation of electrodes

Titanium mesh was cut to be rectangle(25 × 10 × 0.5 mm), and then cleaned in alcohol and in an ultrasonic acetone bath. Mesh TiO_2/Ti electrode was made in 0.5 mol/L H_2SO_4 (Ma, 1998) by anodisation of titanium, in which a titanium mesh and a copper plate with same size were used as an anode and as a cathode respectively. The anodisation process was conducted in two stages, in the first stage, the current had been constantly 1A from the beginning of the oxidation until reaching a designed voltage(e.g. 120 V, 140 V, 160V or 180 V), in the second stage, the designed voltage as the voltage of anodisation was maintained until the end of anodisation. The whole anodisation lasted for 10 minutes. The freshly generated TiO_2/Ti mesh electrode was rinsed by distilled water and then dried in an oven at 105℃ for half an hour.

1.3.2 Photoelectrocatalytic oxidation reaction

A 10 ml aqueous dye solution with RB 20 mg/L in concentration was put into the reaction, then the potentiostat was opened and a certain bias between an anode and a cathode was exerted, air was supplied to the system and electromagnetic stir was carried out, the UV-lamp was opened. The samples were analyzed at a certain interval of time.

1.3.3 Photocatalytic oxidation reaction

A 10 ml aqueous dye solution with RB 20 mg/L and a certain proportional TiO_2 powder were put into reactor, and then electromagnetic stir was carried out for 10 min, air was supplied to system and UV-lamp was opened. The samples were analyzed at a contain interval of time.

2 Results and discussion

2.1 Properties of TiO_2/Ti photoelectrode

The morphology of the titanium mesh and morphology of TiO_2 film prepared in some designed voltages were examined by SEM(Fig.3). It could be observed that the surface of TiO_2 film was rougher than the surface of titanium mesh and was microporous, the pore size increased with the raise of the designed voltage, when the designed voltage raised from 120 V to 180 V, the micropore size measured by SEM increased from 17 nm to 60 nm.

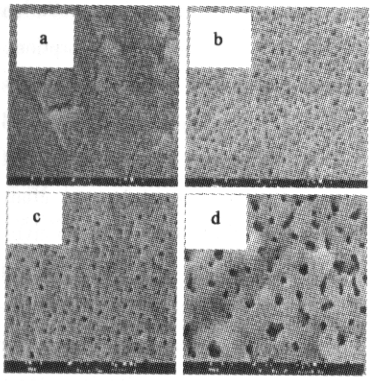

Fig. 3 SEM of TiO_2 electrodes prepared under different voltages
a. Ti; b. 120 V; c. 160 V; d: 180 V

Both the raw titanium-mesh and the TiO_2 electrode prepared using the different voltage were determined ex-situ by Raman spectroscopy(Fig.4). The results showed that the absorption peak of the crystalline TiO_2 strengthened obviously with the raise of the voltage in the anodisation. The crystalline TiO_2 in the anatase form was dominant from 120 V—160 V, while the crystalline TiO_2 in the rutile form appeared obviously in 160 V and the fraction of rutile increased with the raise of the voltage.

The efficiencies of PEC degradation of RB using the electrodes prepared under different design voltages were different(Fig.5), the efficiency using the electrode prepared under design voltage 160 V was better than those using other above electrodes.

Which indicated that the PEC efficiency of dye was related to the properties of the film electrodes, this problem need to make further investigation. The film electrodes prepared in 160 V were used to depredate RB in all following experiments photocatalytic and photoelectrocatalytic degradation.

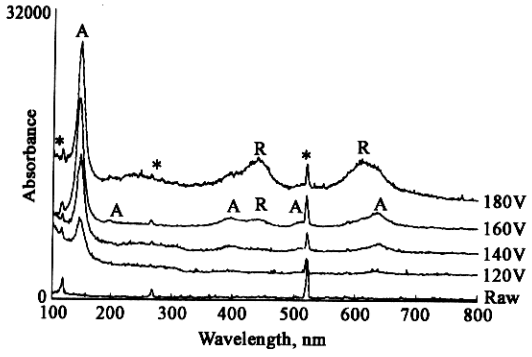

Fig. 4 Raman spectroscopes of raw Ti and TiO_2 electrodes prepared under different voltages
A. anatase TiO_2; R. rutile TiO_2

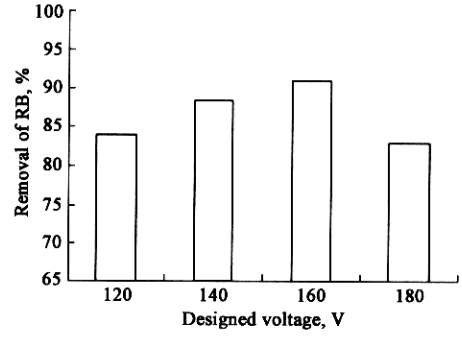

Fig. 5 Removal of Rose Bengal using TiO_2 electrodes prepared under different voltages

2.2 PEC degradation of Rose Bengal

The temporal evolution of the spectral changes taking place during the photoelectrocatalytic degradation of RB was displayed in Fig. 6. Rose Bengal showed a major absorption band at 550 nm, and the position of major absorption band did not change obviously with irradiation time. The inset in Fig.6 shows the change of RB absorbance in the position of major absorption band with irradiation time, the absorbance of RB decreased by ca. 70% for 0.5 h of UV-light irradiation, the absorbance decreased by ca. 80% for 1.0 h.

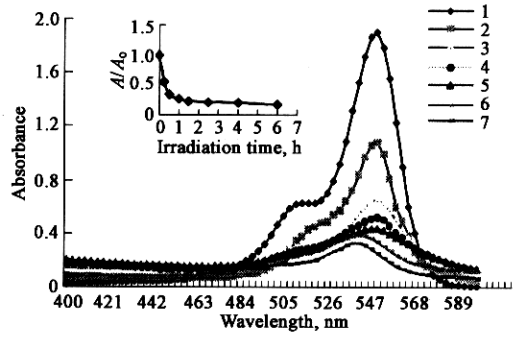

Fig. 6 UV-vis spectral changes of RB as a function of irradiation time; inset: the changes of RB absorbance with irradiation time

2.3 Adsorption of RB on the surface of electrode and effect of bias on PC oxidation

The change of RB concentration under different conditions is shown in Fig. 7. The maximum

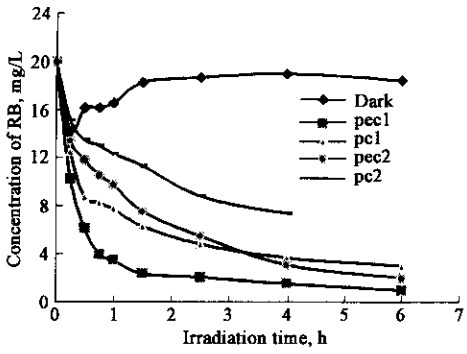

Fig. 7 Degradation of RB with time under different conditions

PEC1 and PC1: light intensity was 2.2 mW/cm^2; PEC2 and PC2: light intensity was 1.3 mW/cm^2; bias in PEC oxidation was 0.6 V

adsorption of RB in the dark was about 30% for irradiation 15 min, then the RB adsorbed on electrode went desorption. When the equilibrium between adsorption and desorption was established for irradiation 1.5 h, the concentration of RB decreased by ca. 15%, it reflected that the adsorption of RB on the surface of film electrode was strong. Many researches gave strong evidence that the photocatalytic reaction took place on the catalyst surface, not in the bulk of the solution(Matthews, 1990). The strong absorption of dye on the semiconductor surface was one of important criteria for an efficient charge transfer(Kamat, 1989). So the strong absorption of RB on the film electrode surface may be benefit to the photocatalytic reaction.

The effect of bias on photocatalytic degradation of RB was vary obvious, the rate of RB degradation increased obviously under bias, especially for first 1 h, the bias made the removal of RB increase by ca.50% in comparison with no bias.

The change of RB concentration under different biases is shown in Fig.8. The results indicated that only a slight difference appeared mainly in the first few hours. Above results indicated that the effect of applying a bias between the electrodes is more important than the difference of the voltage applied.

2.4 The mineralization extent of RB in PEC oxidation

The change of removals of RB and TOC in PEC oxidation with irradiation time is shown in Fig.9. The removal of RB in overall PEC oxidation was almost larger than that of TOC, which indicated that some intermediates were produced. Especially, the amount of intermediates was larger in first few hours. The removal of TOC was ca.90% for irradiation 6 h, it indicated that RB was mineralized basically. The efficient mineralization of RB might be related to properties of TiO_2/Ti mesh electrode, such as larger surface area, excellent conditions of adsorption and substance transfer.

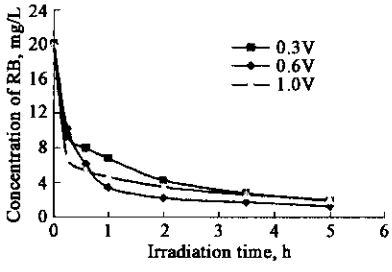

Fig.8 Effect of different biases on degradation of RB PEC oxidation

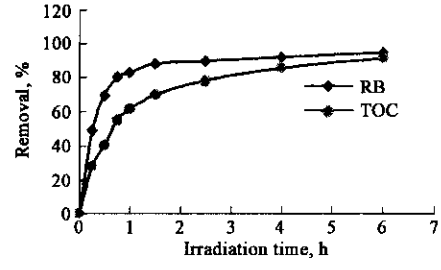

Fig.9 Removal of RB and TOC as a function of irradiation time

2.5 The comparison between PEC oxidation and PC oxidation in TiO_2 suspension

In order to understand the effect of PEC oxidation further, the comparison between PEC oxidation and PC oxidation in TiO_2 suspension with different TiO_2 concentrations of 0.1%, 0.2%, 0.3% and 1%, under otherwise identical experimental condition, was conducted. Several experimental results indicated that the rate of photocatalytic degradation of many organic contaminants fitted the Langmuir-Hinshlwood kinetics(Pruden, 1983; Matthews, 1988; Ollis, 1984). When the initial concentration of organic

contaminants was very small, the Langmuir-Hinshlwood rate form reduced to the apparent first-order kinetics form.

The results in Fig.7 and Fig.8 indicated that degradation of RB in PEC oxidation followed apparent first-order kinetics. The values of rate constant and regression coefficient are listed in Table 1.

Table 1 Values of apparent first-order rate constant (k) and regression coefficient (r) RB in PEC degradation and in dispersions with various loadings of TiO_2

TiO_2, %	k, min^{-1}	r
0.1	0.0141	0.9968
0.2	0.0183	0.9922
0.3	0.0216	0.9933
1.0	0.0566	0.9781
PEC	0.0240	0.9722

The experimental results demonstrated that the reaction rate of RB degradation in the PEC oxidation was faster than that in the PC oxidation with TiO_2 concentration below 0.3%, but not as fast as that in the PC oxidation when TiO_2 concentration such as 1% used in TiO_2 suspension can achieve a higher reaction rate, the separation difficulty would be a factor to consider as possibly limiting. Actually, the concentration of TiO_2 suspension used for most PC oxidation is in the range of 0.1%—0.3%, which means that the PEC oxidation achieved a higher reaction rate than most PC oxidation process. If the degradation rate of RB and its intermediates in PEC oxidation is larger than their adsorption rate on the surface of electrode, the sustainable degradation of organic matters can be continued, and the life-span of electrode can be prolonged although the adsorption of RB on TiO_2/Ti electrode was very strong; otherwise, the accumulation of adsorbate residue on the electrode surface may reduce the efficiency of photooxidation.

3 Conclusions

TiO_2 film on mesh titanium surface was successfully prepared by anodisation, this film had good photocatalytic activity, adsorption property and substance transfer condition. The efficiency of photocatalytic oxidation would be raised obviously when the film was applied in PEC oxidation.

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