PHOTOELECTROCATALYTIC OXIDATION OF RHODAMINE B IN AQUEOUS SOLUTION USING Ti/TiO$_2$ MESH PHOTOELECTRODES

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ABSTRACT

To further improve the photooxidation techniques for water and wastewater purification, a Ti/TiO$_2$ mesh electrode, was successfully prepared by anodizing Ti mesh in 0.5M H$_2$SO$_4$ solution. The structural and surface morphology of the Ti/TiO$_2$ electrode was examined by Raman spectroscopy and scanning electronic microscopy (SEM) respectively. The examination results indicated that its structure and properties were affected by its growth rate in the anodization process, and anatase TiO$_2$ was dominant in its composition. The photocatalytic (PC) oxidation and photoelectrocatalytic (PEC) oxidation of rhodamine B in aqueous solution using the Ti/TiO$_2$ electrode were investigated and compared. The experimental results demonstrated that the PEC oxidation by applying an electrical bias between the Ti/TiO$_2$ electrode and Pt electrode could significantly enhance the degradation rate of rhodamine B compared with the PC oxidation. It was found that the best performance of PEC oxidation was achieved by applying the electrical bias of 0.6V. The mechanism of rhodamine B degradation in the PEC process was discussed by studying the changes of absorbance spectrum and proton nuclear magnetic resonance spectroscopy of rhodamine B during the PEC degradation. The experimental results illustrated that both de-ethylation and chromogen destruction of rhodamine B under UV-light irradiation in the PEC degradation took place simultaneously.

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Keywords: Titanium mesh; anodization; titanium dioxide; photoelectrocatalytic oxidation; rhodamine B

INTRODUCTION

Titanium dioxide (TiO_2) as a photocatalyst has been widely studied in the field of photo-catalysis because of its favorable physical and chemical properties, its high stability and the fact that it is cheap and easily available (1-4). Although the technique is gradually nearing the stage of pre-industrial application, there are still fundamental problems concerning the efficiency of photo-catalysis that need to be solved. Firstly, TiO_2 is a high band gap ($E_g \approx 3.2eV$) material that can only be excited by high energy UV radiation with a wavelength of no longer than 387.5 nm. This practically rules out the use of sunlight as an energy source for the degradation because a significant part of the solar energy reaching the earth surface lies in the visible region (5). Secondly, the low rate of electron transfer to oxygen and the high rate of recombination between electron/hole pairs result in a low quantum yield rate and also a limited photo-oxidation rate (6). Up to now, photocatalysis studies have focused on seeking an effective way to eliminate the recombination of electrons and holes by increasing the charge separation, and also to extend the wavelength range response by photosensitization. The photoelectrocatalytic (PEC) oxidation using a Pt electrode coated with TiO_2 film was first used as a working electrode in the 1982 (7), in which an electrical bias was applied between anode and cathode, and the photogenerated electrons on TiO_2 were driven away. The process can prevent charge recombination and results in an extension in lifetime of the active holes. Subsequently, a number of studies demonstrated the efficiency of PEC oxidation in organic degradation. Vindogopal and his group successfully proved that the photocatalytic oxidation efficiency could be enhanced by applying an anodic bias to a TiO_2 particulate film electrode on conducting glass plate to degrade 4-chlorophenol, whiles the platinum rod acts as a counter electrode (8). In recent years, several studies of degrading formic acid, amino acids and 4-chlorocatechol have been conducted by other researchers (9-11). In their studies, the photoanode was prepared by coating a conducting glass, which was initially covered with indium tin-oxide, with TiO_2. However, it was found that electron mass transfer between the TiO_2 film and supporting carriers was not very efficient due to a poor connection between the two materials. The earlier work on the degradation of rhodamine B confirmed that the hypsochromic shift of the absorbance peak was caused by de-ethylation of rhodamine B, and the de-ethylation occurred in a stepwise manner, the major absorbance band of rhodamine B moved from 552 nm to 539 nm, 522 nm, 510 nm, 498 nm when the ethyl groups of rhodamine B molecule were removed from one group to four groups respectively (13, 14). Ma and Yao in 1998 studied the photodegradation of rhodamine B catalyzed by TiO_2 particles coated film under ultraviolet and visible light irradiation simultaneously, and the results indicated that the maximum absorption of the rhodamine B solution decreased gradually with irradiation time and no peak shift was observed (15). Wu and his co-workers in 1998 investigated the photocatalytic degradation of rhodamine B under visible light irradiation in aqueous TiO_2, and the results showed that both de-ethylation and degradation of rhodamine B took place in the presence of TiO_2 particles, and de-ethylation predominated during the initial irradiation period(16).

In this study, a Ti/TiO_2 mesh electrode was produced by forming a microporous TiO_2 film on Ti mesh in an anodization process, and rhodamine B was used as a dye chemical for photooxidation study under UV irradiation. The objective of this research was to investigate the electrochemistry-assisted photocatalytic activity and properties of TiO_2 film on the mesh electrode in the degradation of rhodamine B to provide an experimental base for further study and practical application in water and wastewater treatment.

EXPERIMENTAL

Materials

Titanium (Ti) 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. The rhodamine B (Tetraethyl rhodamine), was purchased from the Sigma Chemical Co. The molecular structure of rhodamine B is shown in Figure 1, in which the main groups of its structure are labeled with a, b, c, d, e, and f. Other chemicals were of analytical reagent grade and used without further purification. Doubly distilled water was used throughout this study.

[Figure 1]

Equipment

A bench-scale photoreactor system as shown in Figure 2 consisted of a cylindrical borosilican reactor, a 20W UV lamp (NEC T10 BLACKLIGHT) with a maximum UV irradiation peak at 365 nm, and a potentiostat (ISO-TECH 1PS 1810H). The photoreactor has an effective volume of 400 ml, in which two electrodes of Ti/TiO_2 mesh electrode (50 mm × 10 mm) as anode and Pt wire electrode (40 mm in length with a 0.4mm diameter) as cathode were placed in parallel and connected with the potentiostat.

[Figure 2]

Preparation of Ti/TiO_2 Mesh Electrodes.

A large piece of raw Ti mesh with a thickness of 0.5 mm was cut into small rectangle pieces of 25 mm × 10 mm, which were then cleaned with alcohol and acetone solution respectively. The treated Ti mesh and a copper (Cu) plate with the same size were submerged in 0.5M H_2SO_4 solution and an electrical current was applied between the Ti mesh and Cu plate using a laboratory-made DC power supply with a maximum potential of 200V. An anodization process was conducted in two stages, in which the galvanostatic anodization with a constant current density of 100 mA.cm^{-2} was first performed until a designated anode-to-cathode voltage (120V, 140V, 160V and 180V) was reached. Then the constant voltage was maintained until the anodization process completed. In the meantime, the current intensity was decreasing gradually. Since significant heat was generated during the anodization process, the temperature of H_2SO_4 solution increased from 22-24 °C (room temperature) to 36-40 °C. The freshly generated Ti/TiO_2-mesh photoelectrode was then rinsed by distilled water and dried at 105^{o}C in an oven for half an hour. Before the Ti/TiO_2 mesh electrode was used for photooxidation study, its structural and surface morphology were examined and studied using Raman spectroscopy and scanning electron microscopy (SEM), respectively.

Procedure of PEC Oxidation Experiment

A 400 ml aqueous rhodamine B solution with initial concentration of either 5 mg.l^{-1} or 20 mg.l^{-1} was used in experiment. Firstly, the removal of rhodamine B using the Ti/TiO_2 film electrodes prepared under different designed voltages were compared for 3.5 hr of UV-light irradiation, which is as a base of selecting the electrode with good properties. In the study, the removal of rhodamine B was expressed in (Co - C)/ Co × 100%, Co is the initial concentration of rhodamine B, C is the concentration of rhodamine B at time t. Subsequently, at given irradiation time intervals, the samples of rhodamine B solutions were analyzed by a UV-visible spectrometer. The mineralization of organic substance was measured by total organic carbon (TOC) concentration. For comparison, the PC degradation of dye without applying electrical bias potential, degradation of dye in the dark condition with applying electrical bias potential, and the PEC degradation of dye with applying different electrical bias potentials, under identical experimental conditions, were also conducted respectively.

ANALYTICAL METHODS

Structural Analysis

Raman spectroscopy was used to determine the phase of TiO_2 (anatase and rutile) on the mesh electrode. At room temperature, Raman spectra were excited by a 514.5 nm laser line from a CW argon laser (Coherent Innva 70). The laser power was kept at 250 mW to avoid laser annealing of the samples. A 55 mm f/1.8 lens was used for collecting the scattering light which was dispersed and detected using a double grating monochromator (Spex 1403) equipped with a cooled photomultiplier tube (PMT, Hamama-tus R943-2). All spectra were recorded in a small angle scattering geometry. The resolution obtained was expected to be as good as 1 cm^{-1}.

Surface Analysis

Scanning electron microscopy (SEM) (Leica Stereoscan 400i Series) was used to study the surface morphology, average pore size, and pore distribution. High tension was selected at 15 kV.

Light Intensity Measurement.

The intensity of UV irradiation was measured by a Black-Ray UV meter (UVP Inc., model J 221).

Chemical Analyses

The concentration of rhodamine B was determined by high performance liquid chromatography (HPLC), which includes an ISCO model 2350 High Pump, an ISCO RESTEK Pinnacle Octylamine Column (5 μm 250 × 4.6 mm), and a UV detector with a detecting wavelength of 550 nm. The mobile phase used was aqueous solution with 40% acetonitrile.

TOC in wastewater samples was analyzed by a TOC analyzer (SHIMADZU TOC 5000A). The absorbency of rhodamine B in its aqueous solution was also analyzed by the UV spectrometer (MILTON ROY Spectronic Genesys 2).

NMR Analysis

The temporal photodegraded transformation of rhodamine B was also monitored by nuclear magnetic resonance (NMR). The rhodamine B solution samples collected during the photoelectrodegradation reaction were distilled under the reduced pressure to remove the H_2O in samples, and the remaining residues were dissolved in 0.5 ml $CDCl_3$ for NMR measurement.

RESULTS AND DISCUSSION

Structural Analysis of Ti/TiO_2-mesh Electrodes

Raw Ti-mesh and the TiO_2-mesh electrodes prepared using different voltages were examined by ex-situ Raman spectroscopy. Their Raman spectra are shown in Figure 3, in which the peaks representing the anatase and rutile forms of TiO_2 are labeled with A and R respectively. The phonon peaks of anatase were located at 147, 200, 393, 516 and 640 cm^{-1}, whiles the phonon peaks of rutile were observed at 244, 445 and 612 cm^{-1}. The strongest peak of anatase occurred at around 147 cm^{-1} with a narrow shape in all the cases, while other peaks were broader. Up to 140V, the Raman spectra showed that the main anatase peaks were increasing while the applied voltage increased. Above 160V, additional peaks corresponding to the rutile phase of TiO_2 were developed. The spectra also indicate that the anatase phase of TiO_2 was dominant in all the cases with a voltage growth rate of 1.2 $V.s^{-1}$.

[Figure 3]

Surface Morphology of the Ti/TiO_2-mesh Electrodes

From a visual observation, the raw Ti-mesh was silver in color, the Ti/TiO_2-mesh electrode prepared at 120V was sky blue, the Ti/TiO_2-mesh electrode prepared at 140V was light gray to blue, the Ti/TiO_2-mesh electrode prepared at 160V was light gray and the Ti/TiO_2-mesh electrode prepared at 180V was gray. When anodizing titanium, the sparking breakdown voltage that could be achieved was 130V in 0.5M H_2SO_4 solution under a galvanostatic mode anodization, in which the color of the oxide layer changed to gray and surface reflectivity decreased rapidly. The differences in color obtained in oxidized films below the sparking voltage was due to light interference. The morphology of the Ti mesh and Ti/TiO_2-mesh electrodes were examined by SEM and their SEM photos are shown in Figure 4. It was found that the surface of TiO_2 film was microporous and rougher than that of raw Ti mesh. The microspore size measured by SEM was increased from 17 nm to 60 nm, while the applied voltage in anodization increased from 120V to 180V. The earlier work on the titanium anodization indicated that the formation of microspores was attributed to the power dissipation in the barrier oxide layer (12). When anodizing current density was greater than 30 mA cm^{-2} in sulfuric acid, the power dissipated in the barrier oxide layer increased considerably. This current causes local overheating of the oxide, and the cooling of the oxidized anode by the electrolyte becomes insufficient. This higher temperature leads to a higher ionic current probably along grain boundaries, and the oxide may recrystallize and result in a porous surface. With current densities greater than 100 mA cm^{-2}, a fast dissolution of the oxide is believed to occur with the creation of pores, leading to an even rougher surface.

[Figure 4]

Photodegradation of Rhodamine B

The first set of tests was carried out to photodegrade rhodamine B in aqueous solutions for 3.5 hours under UV light irradiation, in which the different Ti/TiO_2 mesh electrodes prepared under different voltages were used. The removals of rhodamine B are shown in Figure 5. The results showed that the PEC degradation rate of rhodamine B using the 160V-electrode was the highest among all the electrodes used. It is indicated that the PEC oxidation efficiency of rhodamine B depended on the characteristics of the Ti/TiO_2 mesh electrodes, including the crystalline texture of TiO_2 and the roughness of surface etc. Therefore, the 160V-Ti/TiO_2 mesh electrode was applied to the following PC and PEC degradation experiments.

[Figure 5]

The light absorbance of rhodamine B sample during the UV-light irradiation is shown in Figure 6, in which rhodamine B demonstrated a major absorption band at 552 nm. The absorbance of the major absorption band decreased by ca. 80% for the first 0.5 hr of UV-light irradiation and decreased by ca. 90% for 1.0 hr. It was also found that the absorbance of the major absorption band shifted from 552 to 500 nm significantly.

[Figure 6]

The second set of tests using the 160V-mesh electrode was carried out in a dark condition and the experimental results are shown in Figure 7. It can be seen that the highest reduction of rhodamine B concentration about 23% occurred at about 1 hour time due to adsorption. Then concentration of rhodamine B recovered gradually due to desorption until a balance was achieved between adsorption and desorption. After 2.0 hr UV irradiation time, the concentration of rhodamine B stabilized with a final reduction of about 15%. The experiment demonstrated a strong rhodamine B adsorption on the Ti/TiO_2 mesh electrode. Actually Many researchers gave strong evidence that this type of PEC oxidation mainly occurs on the catalyst surface, but not in bulk solution. Therefore, the absorption of dye chemicals on the mesh electrode surface plays a very important role in the PEC oxidation reaction.

[Figure 7]

The third set of tests was conducted using the 160V-mesh electrode with applying different electrical potential between the Ti/TiO_2 electrode and Pt electrode. The experimental results are shown in Figure 8. It was assumed the photodegradation reaction of rhodamine B in aqueous solution follows the apparent first order kinetic model as follows:

$$C = C_0 e^{-kt}$$

The calculated values of apparent first-order rate constant, k and regression coefficient, R in the rhodamine B photodegradation with applying different electrical biases are listed in Table 1.

[Table 1]

[Figure 8]

The results in Figure 8 and data in Table 1 indicated that the degradation rates of rhodamine B with applying electrical bias as the PEC degradation were significantly faster than that without applying electrical bias as the PC degradation. It might be resulted from the raise of the quantum yield due to impeding the simple recombination between photogenerated electrons and photogenerated holes in the PEC process. An optimal electrical potential was found to be 0.6V in this experimental condition. To study the effect of pH value on the PEC degradation of rhodamine B solution, the fourth set of tests was carried out with the same light intensity of 4.38 mW.cm^{-2} and applying the electrical bias of 0.6V, but different pH conditions in the range of 2 – 12. The experimental results are shown in Figure 9. The experiment demonstrated that the rhodamine B concentration decreased much faster in acidic solution than that in alkaline solution.

[Figure 9]

Once the photodegradation of rhodamine B was determined by the reduction of rhodamine B concentration, the mineralization of rhodamine B was determined by TOC reduction. The experimental results are shown in Figure 10.

[Figure 10]

The results in Figure 10 demonstrated that the rhodamine B concentration reduced faster than the TOC concentration during the whole reaction. Since the gap between rhodamine B concentration and TOC concentration indicated that the existence of intermediates from rhodamine B degradation, it can be seen that there was a significant accumulation of the intermediates during the first hour of reaction. Then the intermediates were further degradated in the following time and the extent of rhodamine B mineralization increased gradually.

Reaction Mechanism of Rhodamine B in PEC Degradation

The changes of absorbance and the shifting of absorption wavelength during the photoelectrocatalytic degradation of rhodamine B under UV-light irradiation can be clearly seen in Figure 11, which showed that the diminution of the absorbance was simultaneous with the hypsochromic shift in the maximum absorbance. The diminution of absorbance was mainly related to the destruction of the rhodamine B chromogen. In this study, the results in Figure 6 showed that both de-ethylation and chromogen destruction of rhodamine B in the PEC degradation process under UV-light irradiation took place simultaneously, and the diminution of absorbance was significant during the initial irradiation period, while de-ethylation was displayed gradually with prolonging time of UV-light irradiation. The spectra of proton NMR, which depicted the changes taking place in the rhodamine B chromophore, are displayed in Figure 11. Spectra (a - d) illustrated the proton NMR signals of rhodamine B in the PEC degradation at different irradiation times and the corresponding various proton chemical shifts (δ). As the irradiation time lengthened, a sequence of the characteristic signals, which lay at δ 1.3 ($-CH_3$), 3.5- 3.6 ($-CH_2-$), and 6.6-8.4 ppm (aromatic protons), weakened gradually, and the characteristic signal at δ 3.5- 3.6 ppm weakened faster than that at δ 6.6-8.4 ppm. When the above characteristic signals weakened, some new signal peaks appeared simultaneously (the signal at δ 7.3 ppm is that of $CDCl_3$). The results of NMR analysis confirmed that both de-ethylation and chromogen destruction of rhodamine B in the PEC degradation occurred simultaneously, which was consistent with the results of Figure 6. However, de-ethylation was faster than chromogen destruction, the obvious diminution of absorbance during the initial irradiation period in Figure 6 might be partly related to the strong adsorption of the film. The experiment in the latter reaction time showed that some intermediates existed in the PEC degradation of rhodamine B. The new signal peaks at δ 1.1-1.2, 2.2 and 4.7-4.8 ppm might be related to the presence of some groups ($-C-OH$; CH_3-CO-; and $HO-$) respectively, which the new signal peak at δ 3.2-3.7 ppm might be related to the presence of other groups (fatty C–NH and/or $-CH_2-O-$) (17).

CONCLUSION

It has been confirmed that the Ti/TiO_2 mesh photoelectrode has active photoelectrocatalytic properties and excellent adsorption character. The results of the photooxidation experiments show that the anodization film on the titanium mesh surface provides a convenient way to enhance the efficiency of the photocatalytic degradation process. The optimal electrical bias was found to be 0.6V and the rhodamine B photodegraded much faster in acidic condition than that in alkaline condition. Both de-ethylation and chromogen destruction of rhodamine B in photoelectrocatalytic degradation take place simultaneously.

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FIGURE CAPTIONS

Figure 1. Molecular structure of rhodamine B

Figure 2. Sketch of the photoreactor system

Figure 3. Raman spectra of raw Ti- and Ti/TiO_2- mesh electrodes

Figure 4. SEM micrograph of raw Ti mesh and Ti/TiO_2 mesh: A is the raw Ti mesh, B is the 120V Ti/TiO_2 mesh and C is the 180V Ti/TiO_2 mesh

Figure 5. PEC oxidation of rhodamine B using different Ti/TiO_2-mesh elelctrodes with the initial concentration of rhodamine B = 20 mg.l^{-1}

Figure 6. UV absorbance of rhodamine B in the PEC oxidation vs. irradiation time, while light intensity was 4.38 mW.cm^{-2} without applying electrical bias

Figure 7. Reduction of rhodamine B in a dark condition

Figure 8. Reduction of rhodamine B in the PEC oxidation with applying different electrical bias

Figure 9. The photodegradation Rhodamine B affected by pH

Figure 10. The degradation and mineralization of rhodamine B in the PEC oxidation

Figure 11. Spectra of rhodamine B photodegradation in NMR analysis

Table 1. The Kinetic Constants of the First-order Reaction and Regression Coefficient

Bias Applied (V)	k' (min^{-1})	R
0	0.008	0.9864
0.6	0.033	0.9757
1.0	0.027	0.9977
3.0	0.020	0.9979