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A High-Efficient Rotating Disk Photoelectrocatalytic (PEC) Reactor with Macro Light Harvesting Pyramid-Surface Electrode

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A series of pyramid-surface TiO_2/Ti electrodes were proposed, fabricated, and used in a rotating disk photoelectrocatalytic (PEC) reactor to treat rhodamine B (RB) solution. Compared with conventional planar electrode, pyramid-surface electrode exhibited much lower light reflectivity, larger photocurrent, and better treatment efficiency. For samples containing 20 to 150 mg L^{-1} RB, 100– 98% color removal, and 87–30% COD removal were obtained in 150 min using 1/3 (h/w) pyramid-surface electrode, much higher than 98–77% and 48–9% obtained by a conventional planer electrode. The excellent treatment performance attributed to two major reasons: (a) enhanced light harvest resulted from multiple reflections of irradiation light on the pyramid-surface, and (b) enlarged electrode surface area enabling the electrode to carry more TiO_2 catalyst and pollutants for treatment. Experimental results also showed that the pyramid-surface electrode consumed less power and exhibited superior performance when treating high concentration wastewater. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 2448–2455, 2012

Keywords: pyramid-surface TiO_2/Ti electrode, rotating disk photoelectrocatalytic (PEC), reactor, rhodamine B

Introduction

TiO_2 photocatalytic (PC) technology has drawn increasing attention in recent years as a promising green technology to use sun light to treat wastewater directly.[1–3] The researches mainly focused on optimizing the experimental conditions, exploring new photocatalytic materials and designing novel reactors.[4–7] So far, much work has been done to investigate parameters that related to the chemical reactions of the photocatalytic process, such as temperature, oxygen concentration and analytes concentration.[8–10] A series of new catalysts with specific microstructures, like core–shell sphere,[11] cauliflower-like sphere[12] or butterfly wing structure[13] are also developed to improve the phototcatalytic performance.

Designing novel PC reactor is another way to improve treatment efficiency.[14,15] One of the bottleneck problems is how to improve the light utilization efficiency of the system. For a traditional PC reactor, significant amount of irradiation power lost via solution absorption during the process.[16] For example, for a various 20 mg L^{-1} dye solutions, the transmittance, or the portion of light that can be used for PC degradation, is only about 3.1–0.1% when the light path length is 4 cm (the Appendix appears in the supplementary material, see Table A1 in Appendix). In order to solve this problem, a thin film rotating disk PEC reactor has been developed.[16] This reactor combined a highly effective thin-film PEC and a conventional PEC process on a single electrode. The upper part of the round TiO_2/Ti disk photoanode was coated with a thin-film (μm level) of wastewater and irradiated with UV light during treatment. Loss of irradiation power due to absorption by the thin solution film is negligible. The lower part of the disk electrode was immersed in the wastewater to perform conventional treatment. The electrode kept rotating during the treatment, through which the thin aqueous film on the upper part of the electrode was continuously refreshed, and the mass transferred was also enhanced in sample solution. A bias voltage can be added as well to facilitate the separation of photoelectron-hole pairs and, thus, further improve the treatment efficiency. In this system, the possible reactions that occur on the TiO_2/Ti electrode surface are[17]

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{1}$$

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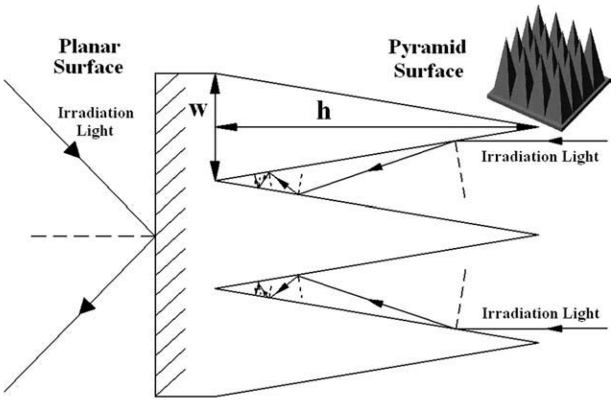


Figure 1. Schematic illustration of single reflection on the planar surface and multiple reflections on a pyramid surface.

$$^{\bullet}\mathrm{OH} + \mathrm{RB} \rightarrow \mathrm{RB}^{*} + \mathrm{CO_2} + \mathrm{H_2O} \tag{2}$$

or

$$\mathrm{RB} + \mathrm{h}^{+} \rightarrow \mathrm{RB}^{*} + \mathrm{CO_2} + \mathrm{H_2O} \tag{3}$$

Equations 1 and 2 suggest that H_2O molecule can be oxidized by TiO_2 holes (h^+) to generate $^\bullet$OH, and then RB is degraded by $^\bullet$OH to intermediate products (R^*), CO_2 and H_2O. Equation 3 suggests that RB can be directly degraded by TiO_2 holes (h^+) to generate intermediate products (R^*), CO_2 and H_2O. Both reaction mechanisms occur quickly on the upper and lower part of the rotating disk when the TiO_2 surface is irradiated by UV light; however the overall reaction is stronger on the upper side of the electrode because more light power is received there.[18]

Loss of irradiation power through planar surface reflection is another problem to hamper light utilization (Figure 1). Anderson et al. reported using a corrugated-plate PC reactor to reduce light reflection;[19,20] however, this design did not avoid the loss of irradiation power by solution absorption, and not all incident light coming from different directions could be fully used.

In this study, we proposed and fabricated a round graded TiO_2/Ti disk photoelectrode with pyramid-surface structure for use in rotating disk PEC reactor. The highlight of the design, as shown in Figure 1, is the incident light can be reflected multiple times on the electrode surface so as to increase the light harvest and improves the light utilization efficiency. Compared with the planar-surface electrode with same diameter, pyramid-surface electrode provides larger surface area, which means more TiO_2 catalyst can be coated on the electrode and more pollutants can be carried and treated during the rotation of the disk. Rhodamine B (RB) was used as the model compound to evaluate the efficiency of this newly designed electrode, and the results were compared with those obtained using a conventional planar photoelectrode.

Experimental

Materials and reagents

Round titanium disk plates (99.6% purity, 75 mm dia.,12 mm thickness) were purchased from Shanghai Hongtai Metal Production Co., Ltd. (Shanghai, China) and employed as the substrates for TiO_2 film coating. Tetrabutyl titanate (Sinopharm Chemical Reagent Co., Ltd., China) was used as the precursor for preparing TiO_2 colloidal suspensions. Rhodamine B (Shanghai Jiaying Chemical Co., Ltd., Shanghai, China) was of commercial grade and used as received. Na_2SO_4 (Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was employed as the supporting electrolyte. All other chemicals were of reagent grade or better quality and used as received. All solutions were prepared in doubly distilled water.

Preparation of the TiO_2/Ti pyramid-surface electrode

In order to better control the conditions of all comparison experiments, we fabricated the round disk electrode one side with pyramid structure. The other side was untreated and used as the planar surface. The pyramid structure was fabricated by an electrical discharge linear cutting machine (DK7732, Jiangsu Taizhou Computer Numerical Control Co., Ltd., China) on one side of the titanium plate. Three different pyramid width to height ratios (w/h, Figure 1), i.e., 1/1, 1/2 and 1/3 were made. Based on the size of the titanium disk plates we used, 2 mm was the most practical width for fabrication; therefore, the pyramid height was 2, 4 and 6 mm. Compared with the planar surface electrode with same diameter (43.5 cm^2, S), the resulted total surface area of these electrodes were 95.5 cm^2 (1/1, 2.2 S), 178.5 cm^2 (1/2, 4.1 S) and 261.0 cm^2 (1/3, 6.0 S), respectively. These three electrodes were then treated by sol–gel and dip-coating process to prepare TiO_2/Ti based photoelectrodes.[16]

TiO_2/Ti rotating disk PEC reactor

The PEC reactor was similar to what we had used in our previous work.[16] The major difference of the setup is that the planar-surface electrode was replaced by a pyramid-surface electrode in this study (Figure 2). The reactor was placed about 3 cm away from an 11 W mercury lamp (Philips, 254 nm), with the TiO_2/Ti disk facing the lamp. The radiation power was maintained constantly at 13 mW cm^{-2} projecting area (Spectra physics power meter, model 407A, U.S.A) during all experiments. The cell and lamp were placed in a wooden box to avoid the influence of natural light and provide protection for the operator, and the electrodes were connected to a DC power supply. The top of the box can be opened for sampling.

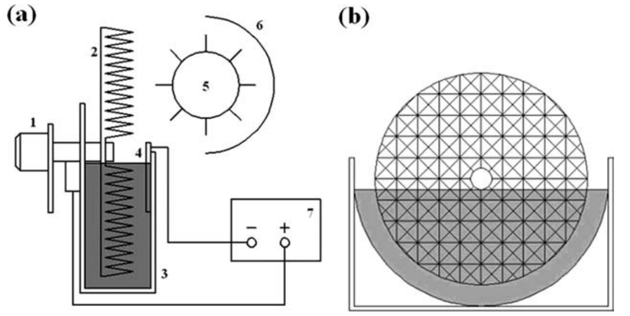


Figure 2. (a) Schematic diagram of the TiO_2/Ti rotating disk PEC reactor.

The figure is not to scale: 1. motor, 2. TiO_2/Ti pyramid-surface anode, 3. electrolytic cell, 4. Cu cathode, 5. UV lamp, 6. aluminum foil, 7. DC power supply. (b) The front view of the TiO_2/Ti rotating disk PEC reactor. The pyramids are not to scale. The cell is filled with sample solution.

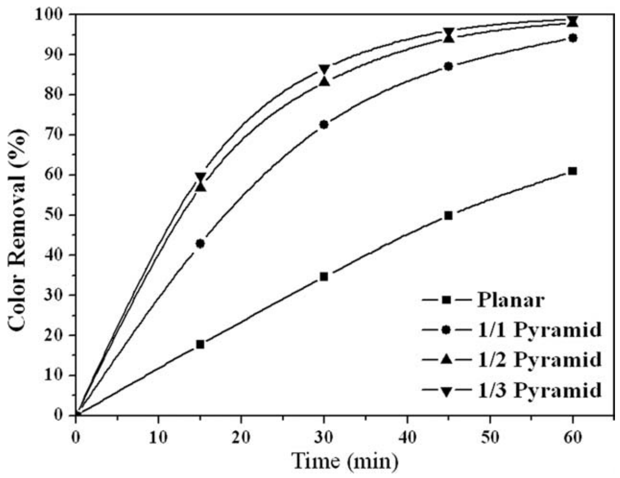


Figure 3. Comparison of the treatment performance of various electrodes.

(CRB = 30 mg L^{-1}, 80 rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4, UV only, no bias voltage).

Degradation experiments

Compared with our previous work,[16] the treatment capacity was scaled up from 55 to 120 mL and the concentration was increased from 20 mg L^{-1} to 30 mg L^{-1}. The effect of the width to height ratio of the pyramid structure on treatment efficiency was investigated first. Electrodes with different width to height ratio, i.e., 1/1, 1/2 and 1/3, were used to treat 120 mL of 30 mg L^{-1} RB solution containing 1.0 g L^{-1} of Na_2SO_4. The disk electrode was rotated at an optimum speed of 80 rpm (Figure A1 of the supplementary material), and no bias voltage was provided. The initial pH of the RB solution was adjusted to 2.50 with 1 mol L^{-1} H_2SO_4 prior to PEC treatment (1 mol L^{-1} NaOH might be needed for fine-tune the pH), because the highest degradation efficiency was obtained at this pH value (Figure A2).

Four sets of method blank experiments were carried out using TiO_2/Ti pyramid anode with 1/3 width to height ratio, which was found to give the best treatment result among all electrodes that had been evaluated (see the following). The experiments were performed in 120 mL of 30 mg L^{-1} RB solution containing 1.0 g L^{-1} of Na_2SO_4. The first set of experiment was to rotate the disk without providing irradiation and bias potential to evaluate the removal of RB via physical adsorption on TiO_2 surface. The second set of experiment was to evaluate the photodegradation of RB, in which the solution was irradiated by UV and agitated by a Ti plate. The third set of experiment was to rotate the TiO_2/Ti disk electrode in solution with UV illumination, but without bias potential to evaluate the effect of photocatalytic (PC) degradation. The fourth set of experiments used the disk electrode as anode (bias +1.6 V) in darkness to perform normal electrolysis degradation. +1.6 V was used because it is the optimum bias potential for the PEC process with 1/3 pyramid-surface electrode (Figure 3a).

In order to compare the performance of the pyramid-surface electrodes and the conventional planar electrode, these two types of electrodes with same diameter (75 mm) were used to treat 120 mL RB solution at different concentration levels (containing 1.0 g L^{-1} Na_2SO_4 electrolyte).

Investigation of factors for improved treatment performance

Two major factors, i.e., enhanced light utilization efficiency resulted from multiple reflections and enlarged electrode surface area, contributed to the improved performance of a pyramid-surface electrode. We should indicate that the enlarged surface area resulted in not only more pollutants being carried for treatment, but also increasing the TiO_2 amount coated on the electrode and improving mass transfer in solution. However, to simplify the model, we combined all contributions together and treated them as the enlarged surface area factor.

Mathematically, the irradiation power received by the planar and the pyramid electrode can be expressed as

$$E_w(mJ) = P\,S\,t$$

where E_w is the received irradiation power (mJ). P is the light intensity (13 mW cm^{-2}), S is the projecting area (43.5 cm^2), and t is the irradiation time (s). For the planar electrode, S also equals to its surface area. In order to quantitatively evaluate the effect of multiple reflections and enlarged surface area, another planar electrode with the same surface area as the pyramid surface electrode should be introduced, and it should receive same amount of irradiation power as the pyramid surface electrode. For example, the surface area of the 1/3 pyramid surface electrode (261.0 cm^2) is six times of that of the planar electrode (43.5 cm^2), or equals to 6S, the light intensity received by the 6S planar electrode therefore has to be decreased by the same fold to keep the total irradiation power received by both electrodes same

$$E_p(mJ) = (P/6)(6S)t = P\,S\,t = E_w(mJ)$$

where E_p is the irradiation power received by 6S planar electrode (mJ). The diameter of a planar electrode with 6S surface area is about 180 mm, which, however, was too big to be fitted into the PEC reactor. To solve this problem, experimentally, we adapted using a planar electrode with the same projecting area as the 1/3 pyramid electrode (S, the back side of the 1/3 pyramid electrode), while it was irradiated for a longer time (6 times than 1/3 pyramid) as an equivalence to the 6S planar electrode. The irradiation power received by the equivalent 6S planar electrode is

$$E_{ep}(mJ) = (P/6)S\,(6t) = P\,S\,t = E_p(mJ) = E_w(mJ)$$

The planar, the equivalent 6S planar, and the 1/3 pyramid surface electrode were used to treat 120 mL of 30 mg L^{-1} RB solutions (1.0 g L^{-1} Na_2SO_4, pH 2.50). The rotating speed was 80 rpm and no bias voltage was applied. Similarly, the 1/1 and 1/2 pyramid surface electrodes and their equivalent 2.2S and 4.1S planar electrodes were also compared under the same experimental conditions.

Analysis

The reflectivity of the pyramid-surface electrode was defined as the ratio of the intensity of the reflected light to the intensity of the incident light. The light intensity was measured using a Nicolet FTIR spectrometer (Nicolet Nexus 870, Thermo, U.S.A) operated at the wavelength from 650 nm to 875 nm. The use of light in visible and infrared range is to avoid the photocatalytic interaction with TiO_2 since the purpose is to measure the physical refection of the light on pyramid-surface. The light source was a tungsten lamp with an incident angle of 30°.

Linear sweep voltammograms of a 10 mg L^{-1} RB solution were obtained at different experimental conditions using an Autolab 4.9 system (Metrohm, Switzerland) with the TiO_2/Ti pyramid-surface electrode as the working electrode; the Pt and saturated calomel electrode as the auxiliary and reference electrode. The results were compared with the voltammogram obtained using a planar electrode with the same diameter.

Dye concentrations were determined by measuring solution absorbance (λ = 563 nm) using a UV–vis spectrophotometer (UV-2102PCS, UNICO, Shanghai). For solutions with high concentration, predilution was needed to decrease the absorbance within the linear range. Chemical oxygen demand (COD) was measured following China National Standard Method GB11914-89.[21] Briefly, 10 mL sample solution was oxidized and refluxed by 5 mL 0.025 mol L^{-1} potassium dichromate and 15 mL H_2SO_4-Ag_2SO_4 for 2 h, then diluted and titrated by 0.005 mol L^{-1} ferrous ammonium sulfate with Ferroin indicator. A blank run using 10 mL doubly distilled water was conducted simultaneously.

Results and Discussion

Performance of various electrodes

All proposed pyramid-surface electrodes had better performance than the planar-surface electrode (Figure 3, same diameter). For the pyramid-surface electrode, the degradation efficiency increased with the increase of the height of the pyramid. For a 30 mg L^{-1} RB solution treated by a planar electrode and pyramid-surface electrodes with width to height ratio of 1/1, 1/2 and 1/3 under UV irradiation for 30 min, but without bias voltage, the color removal by a 1/3 (w/h) pyramid-surface electrode was 87%, much better than that obtained by a planar electrode (35%) and 1/1 (w/h) pyramid-surface electrode (73%); however, it is similar to what obtained by a 1/2 (w/h) pyramid-surface electrode (83%). This is because the treatment almost reached plateau for 1/2 and 1/3 systems at the studied condition. The performance difference of these two systems is more prominent when RB concentration was higher (Figure 4a).

The contributions of the enhanced light utilization and the enlarged surface area were quantitatively evaluated by using the planar, the equivalent planar, and the pyramid-surface electrode receiving the same irradiation power to treat 120 mL of 30 mg L^{-1} RB solutions. As shown in Figure 4a, for a 1/3 pyramid-surface electrode, both enhanced light utilization and enlarged surface area contributed significantly. For example, when irradiation power was 1022 J, the color removal for the planar, the 6S planar, and the 1/3 pyramid electrode was 35, 63 and 87%, respectively. Comparing the results obtained by the 1/3 pyramid surface and the planar electrode, the total color removal improved by 53% (from 35 to 87%), within which, 25% was from enhanced light utilization (from 63 to 87%), and 28% was from enlarged surface area (from 35 to 63%).

For the same color removal, the 1/3 pyramid surface electrode consumes the least irradiation power. When the color removal is 60%, only 510 J irradiation power was used for the 1/3 pyramid-surface electrode, however, 970 J was used for the equivalent 6S planar electrode, and 2000 J was used for the planar electrode, which is nearly 2 and 4 times higher than that used by the 1/3 pyramid-surface electrode.

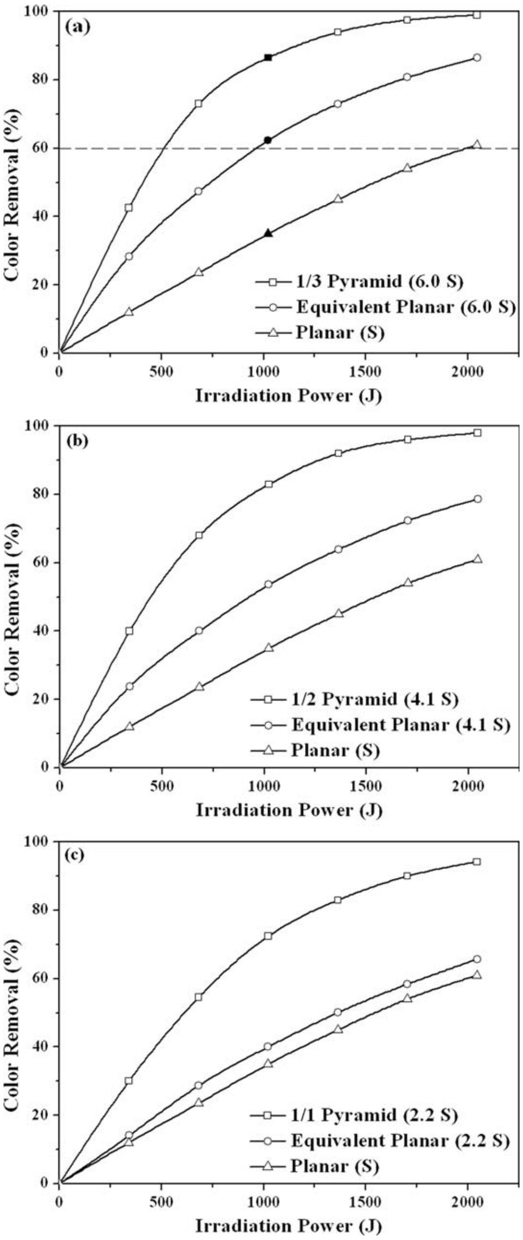


Figure 4. The effect of enhanced light utilization and enlarged surface area on treatment efficiency (a) 1/3 pyramid-surface electrode, (b) 1/2 pyramid-surface electrode, and (c) 1/1 pyramid-surface electrode.

(CRB = 30 mg L^{-1}, 80 rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4, UV only, no bias voltage).

The same phenomena were observed for the 1/1 and 1/2 pyramid-surface electrode system (Figure 4b and c). The quantitative data of contribution of multiple reflections and increased surface area for the pyramid-surface electrodes with different w/h ratio are listed in Table 1. The contribution of multiple reflections decreased with the increase of irradiation power for all pyramid-surface electrodes, suggesting the mechanism works more efficiently when irradiation power is low in that all light (direct and reflected) can be fully utilized. Meanwhile, when the irradiation power is same, although the absolute color removal of 1/1 pyramid surface electrode is lower than that of 1/2 and 1/3 pyramid, the contribution of multiple reflection of 1/1 pyramid surface

Table 1. The Contribution of Multiple Reflections and Increased Surface Area for the Pyramid-Surface Electrodes with Different w/h Ratio

	1/1 pyramid			1/2 pyramid			1/3 pyramid		
Irradiation power (J)	Color removal (A, %)	Increased surface area (B, %)	Multiple reflections (C, %)	Color removal (A, %)	Increased surface area (B, %)	Multiple reflections (C, %)	Color removal (A, %)	Increased surface area (B, %)	Multiple reflections (C, %)
340	30	47	53	40	59	41	43	65	35
681	55	53	47	68	59	41	73	65	35
1022	72	55	45	83	65	35	87	72	28
1362	83	60	40	92	70	30	94	78	22
1703	90	65	35	96	75	25	98	81	19
2044	94	70	30	98	80	20	99	87	13

Experimental condition: 30 mg L^{-1} BR, 80rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4, no bias potential, UV radiation
(A) Total color removal by 1/1, 1/2, 1/3 pyramid-surface electrode;
(B) Proportion of color removal by increased surface area in total color removal;
(C) Proportion of color removal by multiple reflections in total color removal.

electrode is higher than those of others. This is because the surface area factor is more important for electrodes with a much larger surface area.

Characteristics of the pyramid-surface electrodes

One of the important features of the newly designed electrode is the improved light utilization resulted from multiple light reflections on the pyramid-surface. The measured light reflectivity of the pyramid-surface electrodes (<0.001) is significantly lower than that obtained by a planar electrode (0.306) (Figure 5), suggesting the effectiveness of the pyramid structure on light harvest.

The I-V response was investigated by linear sweep voltammetry of a 10 mg L^{-1} RB solution with 1/3 (w/h) pyramid-surface electrode under UV irradiation and bias ranging from $-$ 0.2 V to +1.6 V. The photocurrent increased with the increase of bias voltage, and the photocurrent of the 1/3 pyramid-surface electrode is roughly three times higher than that of the planar electrode (Figure 6). This is mainly because multiple light reflections by the pyramid-surface increased the yield of photoelectron.

Treatment of RB solution by different process

In a TiO_2/Ti PEC process, RB may be degraded or removed under various pathways including TiO_2 adsorption, photodegradation, photocatalysis (PC), electrolysis, and photoelectrocatalysis (PEC). The degradation of RB evaluated by color removal under the aforementioned conditions is shown in Figure 7. Almost no RB was removed by adsorption and electrolysis. Approximately 5% of RB was removed by photodegradation and 85% by PC in 30 min. The best results were obtained by the PEC process offering 92% color removal within the same time frame. Compared with the PC process, the bias voltage employed in PEC process can improve the separation of photoelectron-hole pairs and thus further enhance the light utilization efficiency.[22] However, from a practical point of view, the bias voltage may be not necessary for the real world application since total color removal can be achieved in a longer time frame without the bias as well. This demonstrated again that the proposed technique is very environmentally friendly.

Pyramid-surface electrode vs. planar electrode

The treatment efficiencies obtained by a 1/3 (w/h) pyramid-surface electrode and a planer electrode were quantitatively evaluated and compared. These two electrodes were used to treat individual RB solutions with concentrations ranging from 20 to 150 mg L^{-1}. The results of color and COD removal are listed in Table 2. In the investigated concentration range, PEC with 1/3 pyramid-surface electrode removed total color by 100– 98% and COD by 87– 30%in 150 min, respectively, which is much better than 98– 77% and 48– 9% obtained with a planar electrode under the same experimental conditions.

The pyramid-surface electrode is found to be particularly good at treating high-concentration wastewater. We should point out here that although the percentage color and COD removal decreases with the increase of RB concentration (Table 2), the absolute quantities of RB removed by per unit projecting area of both electrodes increase with the increase of RB concentration. For a 1/3 pyramid-surface electrode,

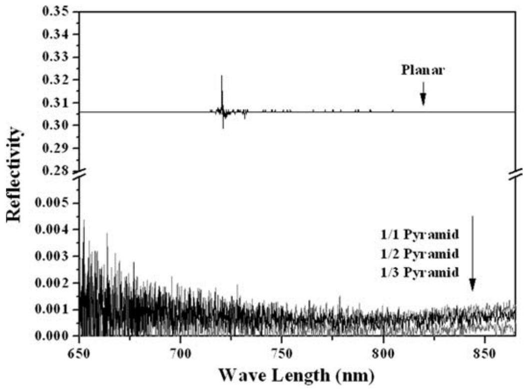


Figure 5. The reflectivity of pyramid-surface electrode with different width/height ratio.

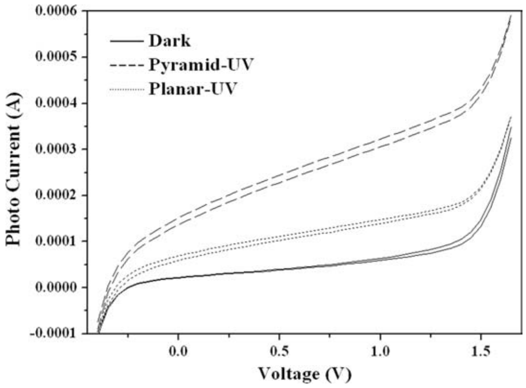


Figure 6. Linear sweep voltammogram obtained by a 1/3 pyramid-surface electrode in a 10 mg L^{-1} RB solution.

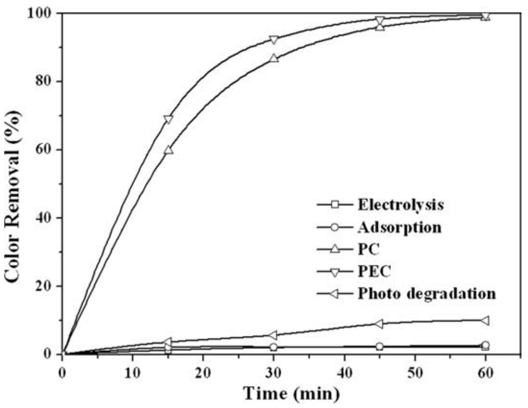
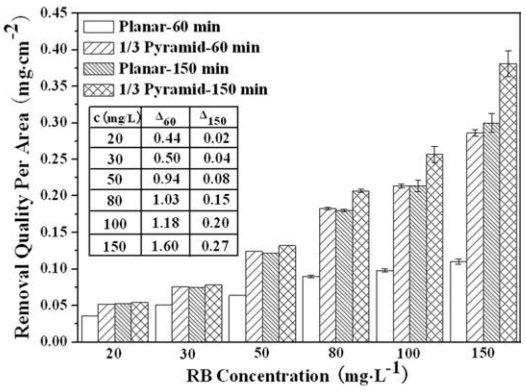


Figure 7. Decolorization of a 30 mg L^{-1} RB solution with the 1/3 pyramid-surface electrode operating at different processes (80 rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4): adsorption (disk in dark without bias); photodegradation (UV irradiation only, disk without TiO_2 coating); PC (disk under UV irradiation without bias); electrolysis (disk in dark with bias, V = + 1.6 V); and rotating disk PEC (TiO_2/Ti disk under UV irradiation with bias, V = + 1.6 V).

the removing rate was 0.381 mg cm^{-2} when treating 150 mg L^{-1} RB solution for 150 min, which is much higher than 0.054 mg cm^{-2} when RB concentration was 20 mg L^{-1}. Additionally, the higher the RB concentration, the better the pyramid surface electrode performed than the planar electrode. Such an improvement was quantitatively expressed as improvement rate (Δ)

$$\text{Improvement rate } (\Delta) = (A - B)/B$$

where A is the quantity removed by the 1/3 pyramid-surface electrode, and B is that removed by the planar electrode under the same condition. When RB concentration increased from 20 mg L^{-1} to 150 mg L^{-1}, the improvement rate increased from 0.02 to 0.27 in 150 min, and from 0.44 to 1.60 in 60 min (Figure 8). When the treatment time is shorter, the advantage of pyramid-surface electrode is more significant than the planar electrode, the absolute quantity of RB removed by the pyramid-surface electrode in 60 min is much higher than that by the planar electrode in the same time frame, and is similar to what obtained by the planar electrode in 150 min.



c (mg/L)	Δ_{60}	Δ_{150}
20	0.44	0.02
30	0.50	0.04
50	0.94	0.08
80	1.03	0.15
100	1.18	0.20
150	1.60	0.27

Figure 8. Absolute quantity of RB removed by each unit (cm_2) projecting area of the 1/3 pyramid-surface and the planar electrode.

(The volume for all solutions was 120 mL, and treatment time was 60 and 150 min, bias potential + 1.6 V, 80 rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4, UV, the error bar for lower concentration is too low to be seen.)

Conclusion

TiO_2/Ti photoelectrode with pyramid structure was fabricated and used as the anode in a rotating disk PEC reactor for the first time. Using this electrode not only minimized the loss of irradiation power by solution absorption, but also significantly enhanced the light harvest. Experimental results showed the excellent performance of the pyramid-surface electrode system and demonstrated the feasibility of the technique. Low-energy consumption and the capability to treat high-concentration wastewater make it a very attractive choice for real world application.

Table 2. Treatment of RB Solution by 1/3 Pyramid-Surface Electrode and Planar Electrode

	Color Removal in 150 min (%)		COD Removal in 150 min (%)	
C_0 (mg L^{-1})	Planar	1/3 pyramid	Planar	1/3 pyramid
20	98	100	48	87
30	97	100	41	77
50	92	100	37	64
80	87	100	32	50
100	83	99	16	38
150	77	98	9	30

Bias potential + 1.6 V, 80 rpm, pH 2.50, 1.0 g L^{-1} Na_2SO_4, UV radiation.

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Appendix

Transmittance (T, %) of 20 mg L^{-1} dye solution at 254 nm

Table A1 shows the transmittance (T, %) of 20 mg·L^{-1} various dye solutions at 254 nm. The transmittance ranges from 6.1 to 29.4% for 1-cm light path length, and 3.1 to 0.1% for 4-cm light path length. These results indicated that significant light lost when using conventional PC technology.

Effect of the rotating speed

Rotating speed of the disk electrode not only is critical for mass transfer but also affects the thickness of the aqueous film coated on the electrode surface. The thickness of the aqueous film coated on a planar electrode surface can be calculated using the following equation

$$\delta = 1.2(V_c)^{0.5}(10^{-4}\text{m})$$
$$V_c = R\omega$$

where V_c is the vertical component of the peripheral velocity at the point where the disk emerges from the water, R is the

Table A1. Transmittance (T, %) of 20 mg L^{-1} Dye Solution at 254 nm

Solution	T* (%)	$T^{\dagger}$ (%)
Acid Fuchsine 6B	25.3	2.1
Allura Red	10.7	0.2
Amaranth	16.2	0.6
Carmine	16.0	0.6
Direct Violet R	29.4	3.1
Weak Acid Green GS	18.9	0.9
Disperse Grey BR	25.4	2.2
Food Lemon Yellow	16.5	1.1
Methylene Blue	18.2	0.9
Methyl Orange	19.8	2.1
Neutral Brown RL	23.1	2.4
Neutral Bordeaux GRL	6.1	0.1
Neutral Orange RL	20.5	1.2
Rhodamine B	17.0	0.8
Sunset Yellow	20.5	1.2
Weak Acid Black BR	26.0	2.2

*In 1-cm quartz cell.
†In 4-cm quartz cell.

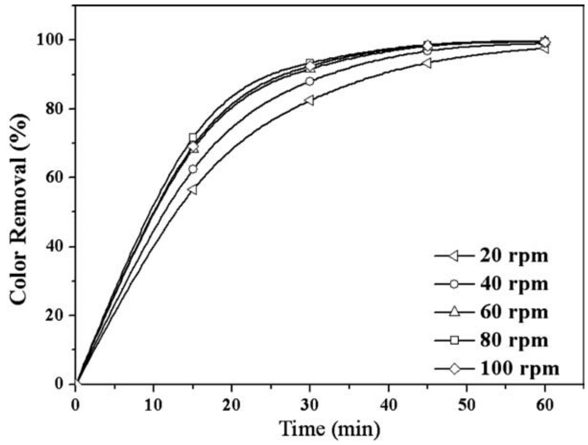

Figure A1. Effect of the rotating speed on color removal by 1/3 pyramid-surface electrode.

C_{RB} = 30 mg L^{-1}, bias potential +1.6 V, pH 2.50, 1.0 g L^{-1} Na_2SO_4, UV.

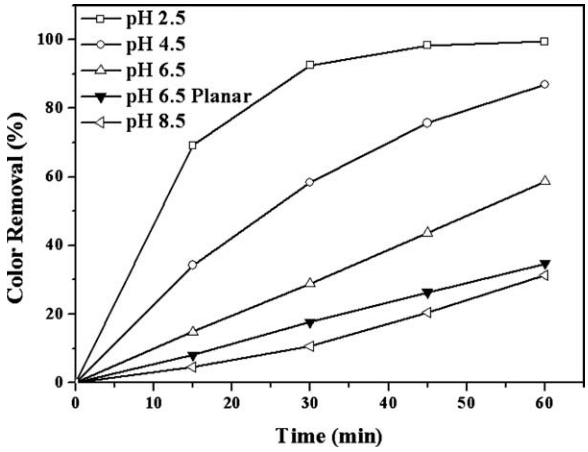

Figure A2. Effect of pH on color removal by 1/3 pyramid-surface electrode.

C_{RB} = 30 mg L^{-1}, bias potential +1.6 V, rotating speed 80 rpm, 1.0 g L^{-1} Na_2SO_4, UV.

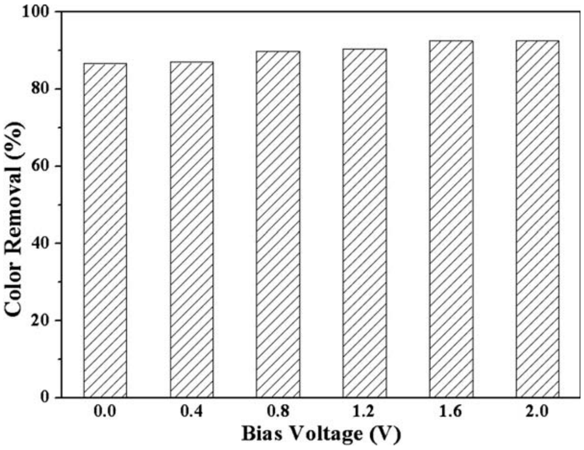

Figure A3. Effect of the bias potential on color removal by 1/3 pyramid-surface electrode in 30 min.

C_{RB} = 30 mg L^{-1}, rotating speed 80 rpm, pH 2.50, 1.0 g L^{-1} Na$_2$SO$_4$, UV.

distance between the disk center to the studied point, and ω is the angular velocity. The thickness of the thin film on the planar electrode is at micrometer level and increases with the increase of rotating speed. The film thickness on the pyramid surface might be slightly thicker because the resistance for liquid down flow along the surface increases.

The effect of rotating speed on treatment efficiency was investigated. In a 30 mg L^{-1} RB solution, the percentage color removal increased with the increase of rotating speed from 20 to 80 rpm; however, it decreased when the rotating speed increased to 100 rpm (Figure A1). Therefore, the optimum rotating speed used in this study is 80 rpm.

Effect of pH

pH is a factor that affects the treatment efficiency. Degradation experiments were performed at different pH by using 1/3 pyramid surface electrode. The percentage color removal increased with the decrease of pH. The best treatment results were obtained when the pH value of the solution was 2.5 (Figure A2). When pH is close to neutral (6.5), 58% color was removed in 60 min with +1.6 V bias voltage. Although it is much lower than that obtained at pH 2.5, it is still better than that obtained by the planar electrode (35%) at the same condition. For industrialization application, a neutral pH might be used though with a compromise of other conditions. In this study, all experiments were carried out at pH 2.5.

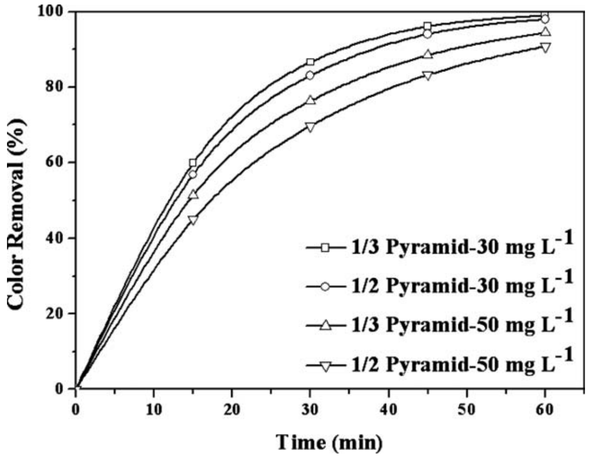

Figure A4. Comparison of the treatment performance of 1/2 and 1/3 pyramid-surface electrodes.

80 rpm, pH 2.50, 1.0 g L^{-1} Na$_2$SO$_4$, UV only, no bias voltage.

Effect of the bias potential

Bias potential is an important parameter in PEC treatment of organic compounds because it facilitates separation of the photoelectron-hole pairs. As shown in Figure A3, the color removal increased with the increase of bias potential up to +1.6 V. No better decolorization was observed with further increase of bias to +2.0 V, which may be due to oxidation of water by photogenerated holes.

Effect of 1/2 and 1/3 pyramid-surface electrode

In Figure 3, color removal obtained by the 1/3 pyramid-surface electrode (87%) is slightly better than that obtained by the 1/2 pyramid-surface electrode (83%), which is because the treatment already reached plateau under the experimental conditions. When RB concentration was increased to 50 mg L^{-1}, however, the difference between the color removal by the 1/3 and the 1/2 pyramid-surface electrode is more prominent (Figure A4).

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