RESEARCH ARTICLE

Efficient photoelectrochemical oxidation of rhodamine B on metal electrodes without photocatalyst or supporting electrolyte

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HIGHLIGHTS

- The efficient PEC degradation of RhB is realized using no photocatalyst.
- The efficient PEC degradation of RhB features the low salinity.
- The PEC degradation of RhB takes place on the anode and cathode simultaneously.

GRAPHIC ABSTRACT

Energy relay structure
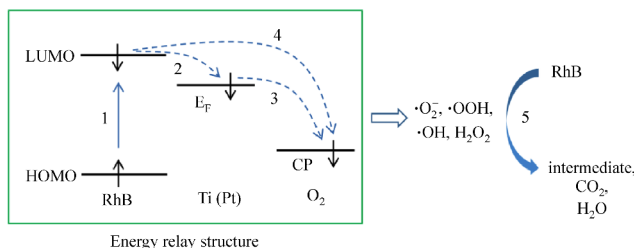
ABSTRACT

We designed photoelectrochemical cells to achieve efficient oxidation of rhodamine B (RhB) without the need for photocatalyst or supporting electrolyte. RhB, the metal anode/cathode, and O_2 formed an energy-relay structure, enabling the efficient formation of O_2^- species under ultraviolet illumination. In a single-compartment cell (S cell) containing a titanium (Ti) anode, Ti cathode, and 10 mg·mL^{-1} RhB in water, the zero-order rate constant of the photoelectrochemical oxidation (k_{PEC}) of RhB was 0.049 mg·L^{-1}·min^{-1}, while those of the photochemical and electrochemical oxidations of RhB were nearly zero. k_{PEC} remained almost the same when 0.5 mol·L^{-1} Na$_2$SO$_4$ was included in the reactive solution, regardless of the increase in the photocurrent of the S cell. The k_{PEC} of the illuminated anode compartment in the two-compartment cell, including a Ti anode, Ti cathode, and 10 mg·mL^{-1} RhB in water, was higher than that of the S cell. These results support a simple, eco-friendly, and energy-saving method to realize the efficient degradation of RhB.

1 Introduction

With the rapid development of modern society, pollution is becoming increasingly severe. Large amounts of wastewater containing organic pollutants are discharged into natural water bodies, threatening both the environment and human health (Forgacs et al., 2004; Martínez-Huitle and Brillas, 2009; Shang et al., 2010). Consequently, it is of great importance to develop cost-effective methods to degrade organic pollutants in wastewater before discharge. Rhodamine B (RhB) is a carcinogenic dye used widely in the paper, paint, leather, textile, and cosmetic industries, and is commonly regarded as a target pollutant in wastewater treatment (Machado et al., 2012).

Electrochemical (EC) oxidation represents a useful wastewater treatment method for degrading organic pollutants, since it is inexpensive, relies on a simple design, and is easy to operate (Chen, 2004). The anode in EC cells can scavenge electrons from organic matter and

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oxidize them into lower-molecular-weight compounds that are either non-toxic or readily degraded into CO_2 and H_2O (Marković et al., 1995). However, EC oxidation possesses several disadvantages, such as side reactions, low electricity utilization efficiency, and high energy consumption, limiting its large-scale industrial application (Feng et al., 2016).

Photocatalysis is widely considered a promising method to degrade organic pollutants because of its non-toxicity, good selectivity, and mild reaction conditions (Gaya and Abdullah, 2008; Chong et al., 2010). Semiconductor photocatalysts can be excited under ultraviolet (UV) or visible light irradiation, generating electrons in the conduction band and holes in the valence band. Organic pollutants adsorbed on the surface of photocatalysts can be oxidized into lower-molecular-weight organic compounds or CO_2 and H_2O by active species, such as O_2^- (Litter, 1999). However, the recombination of hole–electron pairs in photocatalysts markedly reduces the incident light utilization efficiency. Photoelectrocatalysis has been suggested as a solution, where a bias is applied between the photocatalyst-coated anode and cathode to improve the separation of holes and electrons in the photocatalyst (Leng et al., 2005). Recently, photocatalytic and photoelectrocatalytic technologies have been investigated intensively in terms of organic pollutant removal. Obviously, semiconducting photocatalysts (e.g., TiO_2, ZnO, and WO_3) (Okamot et al., 1985; Pekakis et al. 2006; Macedo et al., 2007; Fu et al., 2008; Li et al., 2008) have several intrinsic drawbacks, such as their chemical instability under acidic conditions, low conductivity, narrow spectral response range, and high-probability electron–hole pair recombination (Choi et al., 1994).

Due to the limited fossil fuel availability versus the unlimited light from the sun, light-assisted oxidation of organic pollutants is highly desirable for wastewater treatment. In addition to photocatalysts, organic pollutants can absorb light to generate excitons (i.e., geminate electron–hole pairs). However, due to the large exciton binding energy of organic matter (Knupfer, 2003), the probability of excitons dissociating into hole–electron pairs is low, leading to very inefficient photochemical (PC) oxidation of organic pollutants by themselves. It has been reported that electron transfer from photoexcited citric acid to the metal anode can be very efficient, leading to highly efficient Cr(VI) reduction without requiring photocatalyst (Feng et al., 2016).

Here, based on our understanding that the efficient electron transfer from organic dye to metal electrode can be achieved via photoelectrical synergic effects, the efficient photoelectrochemical (PEC) oxidation of RhB was realized using neither semiconductor photocatalyst nor supporting electrolyte. This research constitutes an important step toward the cost-effective removal of organic pollutants from wastewater.

2 Experimental

2.1 Materials and metal electrodes

Rhodamine B and analytical-grade Na_2SO_4 were obtained from Beijing Chemical Company (Beijing, China) and used as received. Water was purified in the laboratory using a Millipore filtration system with a resistivity of 18.25 MV cm.

A titanium (Ti) mesh electrode (76 mm × 26 mm) was cleaned in acetone, ethanol, and deionized water with an ultrasonic horn for 15 min. After air-drying, it was polished in polishing solution using $HF/HNO_3/H_2O$ (1:3:16 v/v/v) for 15 s. Then, it was cleaned with deionized water and air-dried.

A platinum (Pt) electrode (2 mm × 6 mm) was sanded with fine sandpaper, immersed in dilute nitric acid for 1 h, cleaned with deionized water, and finally air-dried.

2.2 Reaction cell configurations

The single-compartment cell (S cell) was housed in one 7-cm-diameter, 10-cm-high quartz beaker. Four 8-W germicidal lamps (8 W, Hangyun Photoelectric Technology Limited, Beijing) with a main wavelength of 254 nm were placed symmetrically around the quartz beaker as the UV radiation source. The UV light intensity at the center of the quartz beaker was measured as 2.5 mW cm^{-2} using a UVB photometer (UV-B, Beijing Normal University Photoelectric Instrument Plant). Three S cells were designed to investigate RhB oxidation (Table 1).

Table 1   Configurations and rate constants of S cells 1–3

S cell	Anode	Cathode	k (mg·L^{-1}·min^{-1})		
			EC	PC	PEC
1[a]	Ti	Ti	0	0	0.049
2[a]	Pt	Pt	0	0	0.037
3[b]	Ti	Ti	0	0	0.048

Note: [a] The reactive solution was 10 mg·L^{-1} RhB in water; [b] The reactive solution was 10 mg·L^{-1} RhB and 0.5 mol·L^{-1} Na_2SO_4 in water

The two-compartment reaction cell (T cell) was composed of two identical quartz beakers connected via a laboratory-made salt bridge, one housing the anode (anode compartment (AC)) and the other housing the cathode (cathode compartment (CC)). When the AC (CC) was illuminated similarly to the S cell case, the CC (AC) was covered with aluminum foil to prevent illumination. The electrode configurations of T cells 1 and 2 are listed in Table 2.

The open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) in the T cells were measured using a digital multimeter (UT 804; UNI-T, Opava, Czech Republic) to determine the electron transfer from photoexcited RhB to metal.

Table 2 Configurations and photovoltaic parameters of T cells 1 and 2. The AC was illuminated similarly to the S cell case, and the CC was covered with aluminum foil to avoid illumination

T cell	Anode	Cathode	UV Light	
			V_{OC} (V)	I_{SC} (μA)
1 [a]	Ti	Ti	−0.15	−14.6
2 [a]	Pt	Pt	−0.07	−0.5

Note: [a] The reactive solution was 10 mg·L^{-1} RhB and 0.5 mol·L^{-1} Na$_2$SO$_4$ in water

2.3 PC, EC, and PEC oxidations of RhB

The electrodes were immersed in reactive solution for 30 min in the dark to reach adsorption equilibrium. During PC oxidation of RhB, the anode was disconnected from the cathode. During EC oxidation of RhB, illumination was not applied. During PEC oxidation of RhB, the anode potential was fixed at 1.5 V with an EC workstation (CHI 604D; CH Instruments, Austin, TX, USA). A bias of 1.5 V was confirmed to be optimal for the PEC reaction in the designed cells. Variations in the RhB concentration were monitored by measuring the absorbance of sampled solution at a wavelength of 553 nm using a UV–Vis spectrophotometer (UV-3100; Shimadzu, Tokyo, Japan) (Shang et al., 2010). The dependence of the RhB concentration on the reaction time was assumed to follow a zero-order reaction. Thus, the rate constant (k) (mg·L^{-1}·min^{-1}) was expressed as follows:

$$k = \frac{C_0 - C}{t}, \tag{1}$$

where C_0 represents the initial concentration of RhB (mg·L^{-1}) and C represents the instantaneous concentration of RhB at reaction time t (min). The pH values of the solutions were confirmed to be almost unchanged during the PEC oxidation of RhB (Fig. S1).

3 Results and discussion

3.1 RhB oxidation in the S cells

Figure 1 shows the RhB concentration curves over time in S cells 1–3, and Table 1 lists the corresponding rate constants. The RhB concentration remained nearly constant during the first 30 min, indicating that the adsorption equilibrium on the electrodes was reached rapidly and the photolysis of RhB could be neglected under UV irradiation (Fig. S2). In S cell 1, k_{PC} and k_{EC} were almost zero, while k_{PEC} at bias = 1.5 V was 0.049 mg·L^{-1}·min^{-1}, demonstrating that only a combination of UV illumination and bias enabled efficient RhB oxidation. The k_{PEC} of S cell 1 using the Ti anode and cathode was higher than that of S cell 2 using the Pt anode and cathode.

In the photoelectrocatalytic degradation of organic dyes, the supporting electrolyte must make the reactive solution conductive to enable efficient exciton dissociation in the semiconductor photocatalyst. However, high salinity is detrimental to the environment. The current during the PEC oxidation of RhB in S cell 3 using 0.5 mol·L^{-1} Na$_2$SO$_4$ was measured about 30 mA, two orders of magnitude higher than that in S cell 1 without Na$_2$SO$_4$. Meanwhile, S cell 3 had nearly the same k_{PEC} as S cell 1, suggesting that the ion strength had little influence on the PEC oxidation of RhB, that is, the formation of the oxidative species is mainly controlled by light. Therefore, our designed cell represents an advanced, eco-friendly, and cost-effective technology in terms of organic dye removal from wastewater. Moreover, no colorful intermediate products were generated during the PEC oxidation of RhB (Fig. S3).

In addition, PEC degradation of RhB in S cells 1 and 2 was performed with bubbling of N$_2$ into the reactive solution. Introducing N$_2$ severely hindered the PEC degradation of RhB (Fig. 2). S cells 1 and 2 had k_{PEC} values of 0.0043 and 0.0021 mg·L^{-1}·min^{-1}, respectively,
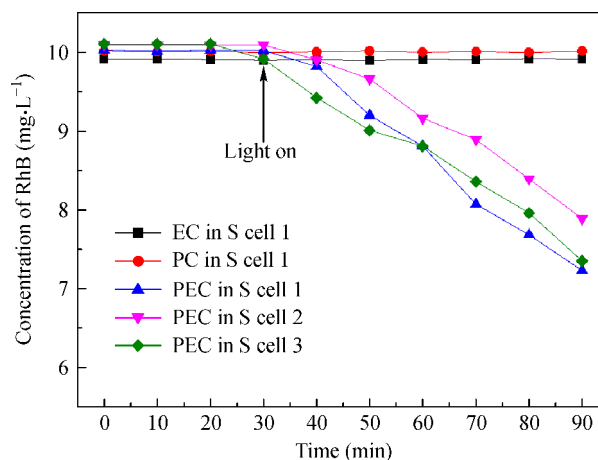

Fig. 1 Variations in rhodamine B (RhB) concentration over time in single-compartment cells (S cells) 1–3 under various oxidation conditions
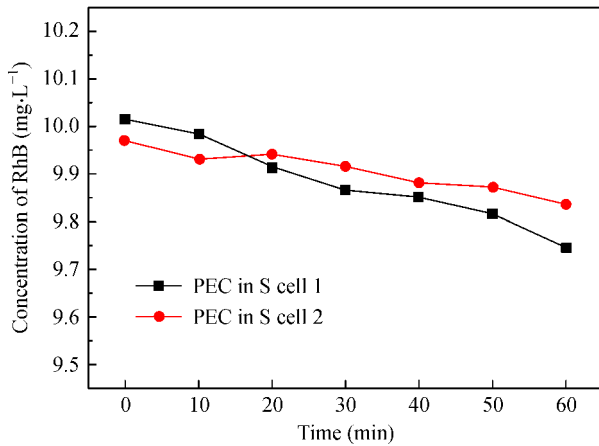
Fig. 2 Nitrogen-bubbled photoelectrochemical (PEC) degradation of RhB in S cells 1 and 2

indicating that O_2 had an important role in RhB degradation in S cells 1 and 2.

3.2 Photoelectrical synergic effect between RhB, the electrodes, and O_2

Table 2 presents a comparison of the photovoltaic parameters of T cells 1 and 2. The weak photovoltaic effects in T cells 1 and 2 were attributed to the photoinduced electron transfer from the lowest unoccupied molecular orbital of the RhB molecule to Ti or Pt (Feng et al., 2016). Negative V_{OC} values indicated that the electron transfer to Ti (Pt) could raise the Fermi level of the Ti (Pt) anode in the AC relative to the Ti (Pt) cathode in the CC. The slightly improved photovoltaic effect in T cell 1 compared to T cell 2 implied that the electron transfer from RhB to Ti was more efficient than that from RhB to Pt. This can be explained by the work function of Ti (4.33 eV) being lower than that of Pt (5.65 eV). Overall, the photoinduced electron transfer from RhB to Ti or Pt is thought to be a fundamental step in realizing efficient PEC oxidation of RhB in S cells 1–3.

Figure 3 shows that the k_{PEC} values in the illuminated ACs of T cells 1 and 2 were almost 0.10 $mg \cdot L^{-1} \cdot min^{-1}$, while the k_{EC} values in the shielded CCs of T cells 1 and 2 were almost zero. Figure 4 displays that the k_{PEC} values in the illuminated CCs of T cells 1 and 2 were 0.053 and 0.065 $mg \cdot L^{-1} \cdot min^{-1}$, respectively, while the k_{EC} values in the shielded ACs of T cells 1 and 2 were almost zero. The efficient PEC degradation of RhB based on the illumination in T cells 1 and 2 indicates that the transfer of photogenerated electrons away from RhB by the electric field is an important step, enabling O_2 to capture these electrons to form active species. If no bias is applied (PC oxidation), the electrons transferred from photoexcited RhB to metal remain immobilized, resulting in a high probability of hole–electron recombination. In other
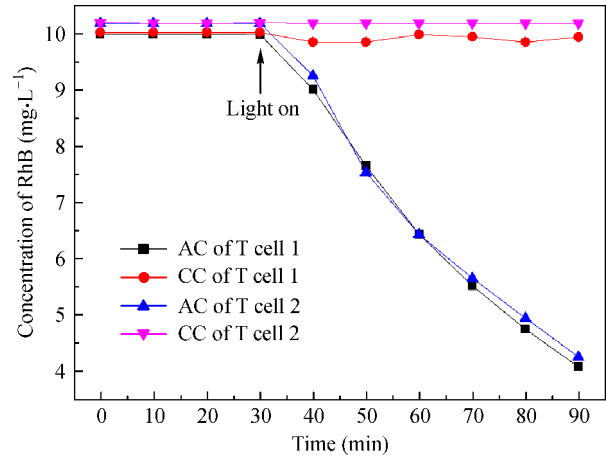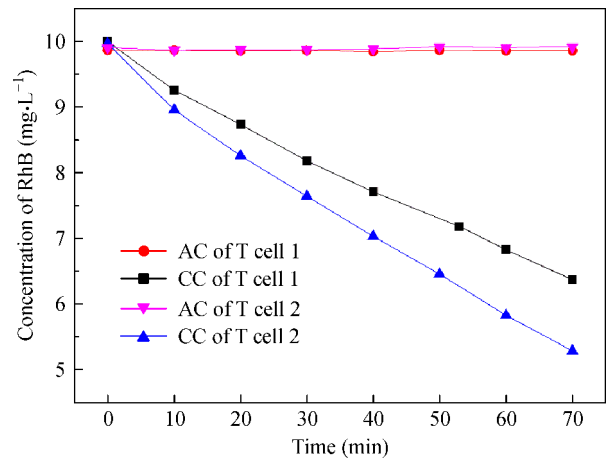

Fig. 3 Variations in RhB concentration over time in T cells 1 and 2 under the condition that the AC was illuminated similarly to the S cell case and the CC was covered with aluminum foil to prevent illumination. The applied bias was 1.5 V and the reactive solution was 10 $mg \cdot L^{-1}$ RhB in water

Fig. 4 Variations in RhB concentration over time in T cells 1 and 2 under the condition that the CC was illuminated similarly to the S cell case and the AC was covered with aluminum foil to prevent illumination. The applied bias was 1.5 V and the reactive solution was 10 $mg \cdot L^{-1}$ RhB in water

words, there is no photoelectrical synergic effect between RhB, metal, and O_2.

3.3 Mechanism of PEC oxidation of RhB

Figure 5 describes the mechanism of the PEC oxidation of RhB. Upon photoexcitation of RhB (Process 1), electrons are transferred from RhB to the metal electrode (Process 2). The electrons transferred to the metal electrode (anode or cathode) are driven away by the electric field and then immediately captured by O_2 (Process 3), forming O_2^-. Process 3 explains the similar efficiencies of PEC oxidation of RhB in S cells 1 and 3, which differed
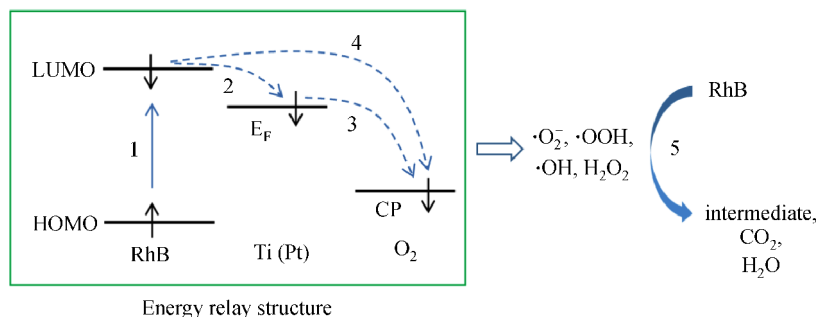
Fig. 5 Diagram describing the PEC oxidation of RhB. HOMO: highest occupied molecular orbital; E_F: Fermi level; CP: chemical potential. Process 1 represents the photoexcitation of RhB. Process 2 represents the transfer of electrons from RhB to the anode (cathode). Process 3 represents the transfer of electrons from the anode (cathode) to O_2. Process 4 represents the electron transfer from RhB to O_2. The relative position of the E_F of the metal to the CP of O_2 can be justified by the fact that oxygen can oxidize Ti and Pt. Due to the role of the metal as the energy stair, the two-step energy transfer (Processes 2 and 3) is much more efficient than the one-step energy transfer (Process 4). Process 5 represents the oxidation of RhB via intermediate products into CO_2 and H_2O

substantially in terms of series resistance. Process 4 is thought to be highly inefficient, because the PC oxidation of RhB in the S cells was nearly zero. By contrast, RhB, the metal anode/cathode, and O_2 form an efficient energy-relay structure, represented by Processes 2 and 3, leading to the efficient formation of active species such as O_2^-, $\cdot$OOH, $\cdot$OH, H_2O_2, etc. (Wei et al., 2012; Sun et al., 2015). Next, RhB is oxidized and ultimately forms CO_2 and H_2O (Process 5).

It is worth noting that the k_{PEC} values in the AC of the T cells were higher than those of the S cells. This was likely because the photoinduced electron transfer from RhB to the anode was partly neutralized by the simultaneous photoinduced transfer of electrons from RhB to the cathode in the S cell, evidenced by the k_{PEC} of S cell 1 being nearly equal to the difference between the k_{PEC} of the illuminated AC and CC of T cell 1. In addition, the k_{PEC} of S cell 2 was almost equal to the difference between the k_{PEC} values of the illuminated AC and CC of T cell 2.

4 Conclusions

Rhodamine B, the metal anode/cathode, and O_2 form an energy-relay structure, leading to the efficient formation of active species such as O_2^- under UV illumination. As a result, the efficient oxidation of RhB is achieved in PEC cells even under low salinity, representing an advanced method compared to conventional photoelectrocatalytic cells, which require high salinity conditions. Thus, we present a simple, energy-saving, eco-friendly, and cost-effective method to remove organic dyes from wastewater.

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