

Photocatalytic and Photoelectrochemically Degradation of Chlorsulfuron herbicide

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Abstract. Photocatalytic and photo electrochemical (PEC) degradation of chlorsulfuron herbicide were studied. Two novel PEC electrodes Ti/IrO₂-Pt-WO₃ (TIW) and Ti/IrO₂-Pt-Ag₃PO₄ (TIA) were designed and some important factors were studied. Lower current density showed lower removal efficiency than higher conditions by electrochemical method. Furthermore, PEC showed higher degradation efficiency than the sum of individual EO and photocatalytic methode.

1. Introduction

The photocatalytic decomposition of various organic compounds in industrial wastewater has been extensively studied, since the pollutants can be oxidized quickly and non-selectively. Among various semiconductors, titanium oxide (TiO₂) has been employed as a typical photocatalyst for both fundamental research and practical applications owing to its excellent stability and high photoactivity under ultraviolet (UV) light. However, its widespread use is limited due to its large bandgap (3.2 eV), which means that it absorbs only UV light [1]. Therefore, there has been a strong demand for new classes of semiconductor materials, and especially those responding to visible light. Considerable effort has been tried to fabricate such photocatalysts, mainly based on TiO₂, by anionic or cationic impurity doping [2], or in combination with smaller bandgap semiconductors [3]. However, in spite of extensive research, most systems have insufficient practical efficiency.

Tungsten trioxide (WO₃) has been studied as one of the best candidates for visible light-driven photocatalysis. It has an indirect band gap with a relatively small energy (2.4–2.8 eV) [4], and many advantages including a deeper valence band (+3.1 eV), strong adsorption within the solar spectrum, stable physicochemical properties, and resilience to photo corrosion effects.

More recently, Ag₃PO₄ semiconductor was reported in photocatalytic applications, which can utilize visible light to rapidly decompose organic contaminants in aqueous solution [5, 6]. Moreover, this novel photocatalyst can achieve a quantum yield up to 90% at wavelengths longer than 420 nm, while most photocatalysts show a comparatively low quantum yield (about 20 %). Umezawa et al. reported the excellent photocatalytic performance of Ag₃PO₄ was attributed partly to the highly dispersive band structure of the conduction-band minimum resulting from Ag s-Ag s hybridization without localized d states [6].

The application of semiconductor photocatalysis and electrochemical oxidation for the destruction of organic contaminants in water has undergone rapid development. Combined electro-oxidation and photocatalysis using a semiconductor film electrode (PEC) has shown great potential compared with individual electrooxidation and photocatalysis [7]. In the combined process, an applied bias potential



not only leads to the electrochemical degradation of target contaminants but also promotes the photocatalysis by driving electrons and providing O_2 . Many active species generated on the electrode surface via photocatalysis will activate the electrode and promote the electro-oxidation of target contaminants [8].

Although the individual electrochemical method could effectively degrade organic contaminants using a Ti/IrO₂-Pt anode, the current density was relatively high. Moreover, without the presence of NaCl, the degradation efficiency was low. Therefore, a novel electrode will be explored via coating WO₃ or Ag₃PO₄ onto the Ti/IrO₂-Pt to form Ti/IrO₂-Pt-WO₃ (TIW) and Ti/IrO₂-Pt-Ag₃PO₄ (TIA) to exhibit a synergetic effect between the electro-oxidation and photocatalysis by sol-gel or electro-deposition methods. Chlorsulfuron (ChS) herbicide was chosen as the model contaminant to evaluate and compare the electrochemical oxidation (EO) under low current density without the presence of NaCl, photocatalytic (PC) and PEC degradation of ChS herbicide using Ti/IrO₂-Pt anode, WO₃, Ag₃PO₄ and TIW, TIA.

2. Materials and methods

2.1. Materials

All chemicals were used as received without further purification. Chlorsulfuron (ChS) standard material (99.0%) used in this study was purchased from WAKO Pure Chemicals Ltd. Japan. 10 mg of ChS was dissolved in 10 mL of methanol (HPLC grade, WAKO Pure Chemicals Ltd. Japan) to be the stock solution, and stored in the dark at 4 °C prior to use. They were diluted with Milli-Q water (resistivity 18.2 MΩ cm at 25 °C) prepared with a water purification system (Purelite PRB-001A/002A) to the desired concentration required for each experiment and or analysis.

A simple cubic electrochemical cell was designed with a working volume of 100 mL (Fig.1). A DC potentiostat (GW INSTEK, GPS-183000) with a voltage range of 0-18 V and a current range of 0-3 A was employed as power supply. A Ti/IrO₂-Pt electrode (TohoTech Company, Japan) of 51.6 cm² (4.3×12 cm²) was used as the anode for the EO and substrate for the PEC. And a Ti electrode with the same area was used as the cathode, and a distance of 1cm between the two electrodes was set. The immersed areas of the anode and cathode in the treated solution were the same at 25 cm².

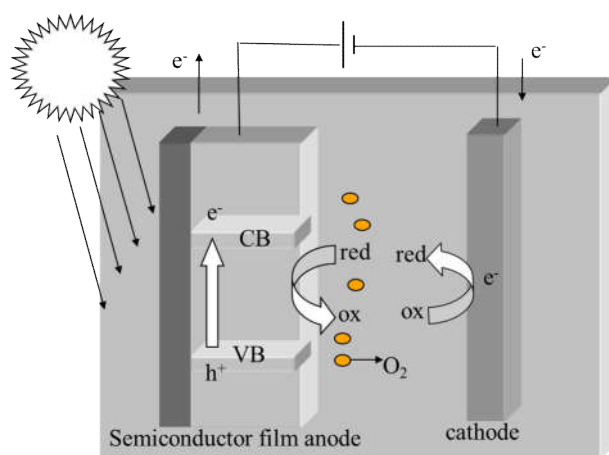


Figure 1. Mechanism and experimental setup for PEC degradation of ChS (red-reduction, ox-oxidation)

2.1.1. Fabrication of Film TIW Electrode, WO₃ was coated onto the Ti/IrO₂-Pt by sol-gel method [9]. Tungstic acid (yellow powder; 0.25 g, 1.0 mmol) was dissolved in a 30% ammonia aqueous solution (0.6 ml) to give a colorless solution containing a little bit of white precipitate (ammonium tungstate). Ethanol (1.0 ml) and PEG (0.78 g) were added to the solution, providing the viscous stable suspension of ammonium tungstate as a precursor paste. And then spin coat onto the Ti/IrO₂-Pt electrode

(1000r/min, 3 times). Finally the electrode was air-dried for 30 min followed by a calcination treatment at 400 °C for 90 min to form a WO₃ film.

2.1.2. Fabrication of Film TIA Electrode, Ag₃PO₄ was coated onto the Ti/IrO₂-Pt by the electrochemical method to form TIA electrode [5]. First, Ti/IrO₂-Pt electrode as the cathode and a piece of Pt sheet as the anode were immersed in a 0.02 mol L⁻¹ silver nitrate solution with 1.0 V d.c. voltage to deposit a bright layer of Ag on the conducting glass surface. Then the anode and the cathode of the d.c. power source were exchanged, and the electrolyte was replaced by a 0.02 mol L⁻¹ sodium orthophosphate solution. The Ag on the surface of the Ti/IrO₂-Pt electrode was gradually oxidized and reacted with orthophosphate anions in situ to form vivid yellow Ag₃PO₄ thin films under a d.c. voltage of 0.8-0.9 V.

2.2. Method

2.2.1. PC experimental procedure, The PC activities of the WO₃ and Ag₃PO₄ were evaluated by ChS degradation in an aqueous solution under a simulated solar lamp (XC-100B, SERIC, Japan), with its 90% energy between 420-750 nm. The light intensity was measured with a photometer (Li-250A, Li-COR, USA), and the values were about 0.7 mW cm⁻². The photocatalysts (0.1 g) were added to an aqueous ChS solution (50 mL, 1 mg L⁻¹) at room temperature in air. And a 100-mL breaker was used as the reactor and was equipped with a magnetic stirrer. Before light turned on, the suspension was magnetically stirred for 30 min in the dark to establish an adsorption-desorption equilibration. Samples were taken from the reactor with different interval (30, 60, 90, 120 min) for analysis.

2.2.2. EO experimental procedure, In the present study, all of the electrolysis experiments were performed under galvanostatic control at different current densities of 0.4, 2, and 4 mA cm⁻², respectively. ChS solution were prepared for electrolysis experiments. In all of the electrolysis processes, 1.5 g L⁻¹ Na₂SO₄ was added into the solution in order to enhance the conductivity of the solution. A 100 mL of synthetic ChS solution (1 mg L⁻¹) prepared with the stock solution and distilled water was transferred into the electrochemical cell, and then the electrolysis began under different current density conditions. Samples were taken from the electrochemical cell with different interval (30, 60, 90, 120 min) for analysis.

2.2.3. PEC experimental procedure, Degradation experiments were performed in an electrochemical cell. The reactor, which contained 100 mL ChS solution (1 mg L⁻¹) under galvanostatic control at different current densities of 0.4, 2, and 4 mA cm⁻², was placed under a simulated solar lamp (XC-100B, SERIC, Japan). In all of the electrolysis processes, 1.5 g L⁻¹ Na₂SO₄ was added into the solution in order to enhance the conductivity of the solution. The light intensity was measured with a photometer (Li-250A, Li-COR, USA), and the values were about 0.7 mW cm⁻². Before the experiment began, the suspension was magnetically stirred for 30 min in the dark to establish an adsorption-desorption equilibration. Samples were taken from the reactor with different interval (30, 60, 90, 120 min) for analysis.

2.3. Analysis

The concentrations of ChS were determined by means of HPLC (Jusco, Japan) with a autosampler model. The column was 5 C18-AR-II, 4.6×150 mm. The flow rate was 1.0 mL min⁻¹ and the injection volume was 50.0 µL. The mobile phase was the mixture of methanol and water (1:1), with pH adjusted to 2.80 by using H₃PO₄. The solution pH was measured by pH/iron meter (Mettler-Toledo AG 8603, Schwerzenbach, Switzerland).

3. Results and discussions

3.1. PC degradation of ChS

As shown in Fig.2, the ChS was stable under the simulated solar light. After 120 min direct photolysis, only 8% ChS was degraded. And the ChS degradation rate increased in the presence of the TIW and TIA film in comparison with the direct photolysis of ChS. About 51.1% and 31.3% of ChS could be removed using the TIA film and the TIW film within 120 min, respectively.

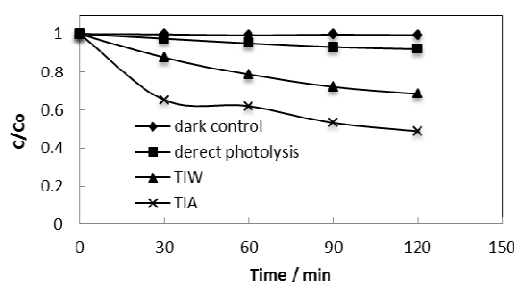


Figure 2. Relative concentration variation of ChS with irradiation time under simulated solar light

The wider band gap of the TIA film than that of the TIW film contributed to a more powerful redox capability. Its porous structure offers more active sites to adsorb water and hydroxyl groups, which capture holes generated by illumination and produce active hydroxyl radicals. The porous structures also offer an advantage in that the diffusion length of the valence band holes formed by the band gap photoexcitation is short, because the electrolyte solution can penetrate into the pores in the whole film. The Ag_3PO_4 photocatalyst can achieve a quantum yield up to 90% at wavelengths longer than 420 nm, while most photocatalysts show a comparatively low quantum yield (about 20 %). Umezawa et al. reported the excellent photocatalytic performance of Ag_3PO_4 was attributed partly to the highly dispersive band structure of the conduction-band minimum resulting from Ag s-Ag s hybridization without localized d states [6]. However, Ag_3PO_4 was slightly soluble in aqueous solution, which decreases its structural stability. In addition, the photocatalytic corrosion of the Ag_3PO_4 makes the by-products, black metallic Ag particles, suspended in the reaction systems and might deposit onto the surface of catalyst, which would decrease photocatalytic activity. This might be the reason why the ChS degradation rate was fast at the beginning but became slower later.

3.2. EO degradation of ChS

Fig.3 shows the concentration variation of ChS at various low current densities of 0.4, 2, and 4 mA cm^{-2} , respectively. And the degradation rate increases as a function of the current density. Furthermore, the degradation rate of ChS slows up with the increase of applied bias. Moreover, nearly no degradation of RhB is observed at current density of 0.4 mA cm^{-2} . The result indicated that without the presence of NaCl, the degradation efficiency was very low, especially at low current density.

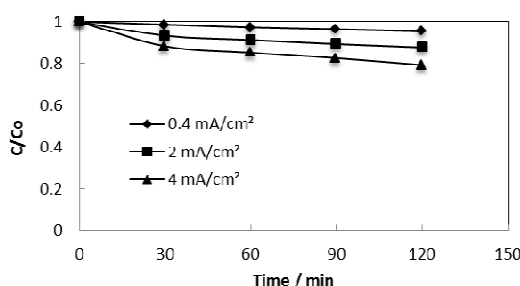


Figure 3. Concentration variation of ChS in EO degradation at various current densities in 1.5 g L⁻¹ Na₂SO₄ solution

3.3. PEC degradation of ChS

PEC degradation of ChS using TIW and TIA was performed at current densities of 0.4, 2, and 4 mA cm⁻². The variation of relative concentration (Ct/C0) of ChS versus function of time is shown in Fig. 4

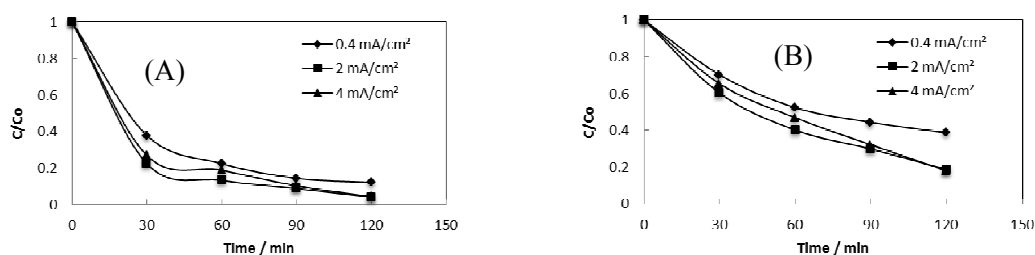


Figure 4. PEC Degradation of ChS under different current densities under the simulated solar light (light intensity, 0.7 mW cm⁻²). (A) TIW film anode, (B) TIA film anode

It is clearly shown that the current densities at 0.4, 2, and 4 mA cm⁻² can promote the photocatalytic degradation effectively. The degradation rate of was increased at the current densities at 0.4, 2 mA cm⁻², while the ChS degradation rate seemed to somewhat decreased at 4 mA cm⁻².

Furthermore, it is observed that the kinetic constants of the PEC process are beyond the sum of the EO degradation or PC process individually. Below current densities of 2 mA cm⁻², the potential increases the photocatalytic degradation rate of ChS by promoting the separation and transfer of photo generated holes and electrons. And the current density can not only separate the holes and electrons but also directly electrolyze ChS. The integrated degradation of ChS was through the direct electro-oxidation and photocatalysis. However, at current density of 4 mA cm⁻², the by-product (H₂) formation reaction may decrease the degradation efficiency.

The TIA film electrode showed higher degradation rate than that of TIW film electrode at the beginning of the experiment. However, the degradation rate by TIA film electrode decelerated subsequently, due to the fact that Ag₃PO₄ is slightly soluble in aqueous solution, which decreases its structural stability. In addition, the photocatalytic corrosion of the Ag₃PO₄ makes the by-products, black metallic Ag particles, suspended in the reaction systems and may deposit onto the surface of the catalyst with decreased photocatalytic activity.

4. Conclusion

Two novel PEC electrodes (TIW and TIA) were designed and some important factors were studied. In this integrative process, PEC showed higher degradation efficiency than the sum of individual EO and PC degradation of ChS. In the combined process, an applied bias potential not only leads to the electrochemical degradation of target contaminants but also promotes the photocatalysis by driving electrons and providing O₂. Many active species generated on the electrode surface via photocatalysis will activate the electrode and promote the electro-oxidation of target contaminants.

Acknowledgments

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