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Heterojunction between anodic $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and cathodic WO_3/W nano-catalysts for coupled pollutant removal in a self-biased system

Tingting Yu^a, Lifan Liu^{a,b,*}, Fenglin Yang^a^a Key Laboratory of Industrial Ecology and Environmental Engineering, MOE, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, Liaoning, China^b School of Food and Environment, Dalian University of Technology, Panjin 124221, Liaoning, China

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ABSTRACT

An anodic $\text{TiO}_2/\text{g-C}_3\text{N}_4$ hetero-junction and cathodic WO_3/W were used to build a self-sustained catalytic fuel cell system for oxidizing rhodamine B or triclosan and reducing NO_3^- -N to N_2 simultaneously. The WO_3 nano-catalyst was formed in situ by heating and oxidizing a tungsten wire in air. Cyclic voltammetry and current-time curves were used to characterize the electrochemical properties of the electrodes and system. Aeration and activation of molecular oxygen by self-biased $\text{TiO}_2/\text{g-C}_3\text{N}_4$ led to the formation of reactive oxidizing species in the fuel cell. The mechanism of simultaneous anodic oxidation of pollutants and cathodic reduction of nitrate was proposed. The spontaneously formed circuit and tiny current were used simultaneously in treating two kinds of wastewater in the reactor chambers, even without light illumination or an external applied voltage. This new catalytic pollution control route can lower energy consumption and degrade many other kinds of pollutants.

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1. Introduction

Electrochemical or photoelectrochemical semiconducting catalysis can be used to oxidize organic or degrade inorganic pollutants in aquaculture wastewater [1], new emerging contaminants [2], dye [3–6] or used for disinfection [7], and is widely studied and used in the catalytic wastewater treatment. It is promising for mitigating environmental pollution problems and lower the energy cost. Yet so far, the undesirable electrons (e^-) and hole (h^+) recombination after the excitation is still a problem. Hetero-junction construction is an effective approach to improve the separation of photo-generated e^- and h^+ [8–14]. The separated e^- and h^+ can be used for decontamination and energy generation. For pollutant degradation, e^- is

used to reduce high valence inorganic pollutants [15] and h^+ or reactive oxygen species (ROS) to oxidize organic pollutants [16,17], or for the simultaneously coupled oxidation and reduction of pollutants [18–21]. In view of this, we need to seek an effective approach to maintain a green ecological system to degrade and remove pollutants. Furthermore, it would be promising to develop a new method to eliminate pollution and recover the electrical energy stored in wastewater simultaneously.

A photo-electrochemical system can reduce the recombination of e^- and h^+ , and it also can solve the problem of low quantum efficiency by catalyst immobilization [22,23]. Due to the different Fermi levels, electrons and holes in the hetero-junction between the anode and cathode are driven by a self-built

* Corresponding author. Tel: +86-427-2631799; Fax: +86-411-84708084; E-mail: lifanliu@dlut.edu.cn

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bias and internal electric field [24,25]. The charge carriers are thus separated and carrier lifetime is prolonged.

A TiO₂ composite with a visible light photocatalyst (g-C₃N₄) to form a heterojunction and enhance the photocatalytic activity was effective due to the separation of e⁻ and h⁺ pairs [26–32]. The conduction band (CB, ~ -1.12 eV vs. NHE) of g-C₃N₄ is more negative than the CB of TiO₂ (~ -0.2 eV vs. NHE), and an interior bias was produced to move the localized e⁻ of g-C₃N₄ to TiO₂. The CB (~ +0.2 eV vs. NHE) of WO₃/W is more positive than TiO₂ and g-C₃N₄. Consequently, an interior bias was produced to move the electrons of the anode through an external circuit to the cathode to reduce inorganic pollutants. Electrons can be trapped by O₂ and be involved in the formation of ROS (such as •O₂⁻). The holes and ROS of the anode can be used for organic degradation in the anode chamber.

Previously, we described an innovative self-biased electrochemical fuel cell system to remove an organic pollutant comprising anodic TiO₂/g-C₃N₄ and cathodic nano-Pt [24]. However, no pollutant was removed or degraded by the cathode. In this work, we expanded and advanced the previous system to develop a new stage. We adopted a WO₃/W cathode which was prepared by a simple method. Interestingly, it utilized the self-bias between the TiO₂/g-C₃N₄ and WO₃/W electrodes to generate a microscopic current without needing light, and it could reduce nitrate. The e⁻ generated from this system can activate O₂ to produce ROS and oxidize rhodamine B (RhB) and triclosan (TCS) also by h⁺ in the anode chamber. Meanwhile, the e⁻ from the TiO₂/g-C₃N₄ anode were transferred and conducted through the external circuit to the WO₃/W cathode to reduce the NO₃⁻-N in the cathode chamber. This system does not use any input of light irradiation or applied voltage to degrade the pollutants. The self-biased system developed is low-cost, and it established an effective way to generate the small current for simultaneous anodic organic degradation, cathodic nitrate reduction and electricity production.

2. Experimental

2.1. Preparation of the TiO₂/g-C₃N₄ anode

Previously, we have prepared the TiO₂/g-C₃N₄ anode [24]. Briefly, g-C₃N₄ was prepared by heating melamine covered in an alumina crucible (heating rate 5 °C/min) and calcined at 530 °C for 4 h. The resulting yellow g-C₃N₄ was ground into a powder for further use. The TiO₂/g-C₃N₄ (photo) anode was prepared by a sol-gel method and dip-coated onto carbon fiber cloth. Typically, 27 mL tetra-butyl titanate was mixed with 23 mL ethanol in a beaker, followed by adding 3.3 mL hydrochloric acid (37 wt%) and 2.7 mL distilled water. Then, 0.5 g g-C₃N₄ was added into this solution. The mixture was kept under magnetic stirring for 1 h, and a light yellow sol-gel was formed. The resulting paste was dip-coated onto carbon fiber cloth (0.5 mg/cm²) and was dried at 105 °C for 5 min. After repeated coating and drying five times, the electrode was transferred into a tube furnace for calcination at 450 °C for 2 h. Finally, the anode was obtained.

2.2. In situ grown WO₃ catalyst on a tungsten wire and characterization of the WO₃/W cathode

First, a tungsten wire (diameter, Φ 0.25 cm $\times$ d 40 cm) was immersed in ethanol for 24 h to remove impurities. Then, it was dried at 60 °C. To grow WO₃ nanoparticles on the tungsten wire, it was heated in an alumina crucible (heating rate 5 °C/min) and calcined at 500 °C for 2 h. The color of the tungsten wire changed from black to pale yellow. The in situ grown WO₃ nanoparticles on tungsten wire were directly used as the cathode.

The morphology of the tungsten wire with WO₃/W was characterized by a scanning electron microscope (SEM, NOVA NANOSEM 450, USA). Cyclic voltammetry (CV) curves were measured from -1 V to +1 V vs. Hg/HgCl₂ at a scan rate of 50 mV/s in different electrolytes (0.05 mol/L formic acid + 100 mg/L NO₃⁻-N, 0.05 mol/L Na₂SO₄) with the use of UV and without. N₂ was sparged through the electrolyte to remove dissolved O₂ before the measurement.

2.3. RhB and TCS degradation

The setup of the system was the same as in our previous report [24]. The TiO₂/g-C₃N₄ anode and WO₃/W cathode were put into the anode and cathode chamber, respectively. For comparing the removal rates with light and without light, a 20 W UV lamp or a 50 W halogen lamp, which supplied UV light or visible light, was positioned beside the reactor vertically, and irradiated the TiO₂/g-C₃N₄ anode and WO₃/W cathode through the quartz glass. The anode and the cathode were divided by a cation exchange membrane (DF-120, Shandong Tianwei Membrane Technology Co., LTD., China) in the middle.

The removal rate of RhB and/or TCS in the anode chamber and NO₃⁻-N in the cathode was compared with UV and without any light. The air aeration rate of the two chambers was controlled by a gas flow meter and kept at 200 mL/min (anode with air, cathode with N₂).

Generally, for adjusting the ionic strength and pH values, 0.02 mol/L NaOH with 10 mg/L RhB (TCS, 100 mg/L) was used as the anolyte (350 mL), and 0.02 mol/L formic acid (FA) with 100 mg/L NO₃⁻-N was used as the catholyte (350 mL). The external resistance was 1000 Ω between the anode and cathode. The tests were studied at room temperature.

2.4. Photo-electrochemical system measurements

Prior to degradation, the system was kept in a dark condition for 2 h to reach adsorption/desorption equilibrium. The solution was sampled every 30 min. The absorbance changes of RhB (TCS) were measured using a 752 UV-Vis spectrophotometer (Shanghai Jinghua Technology Instrument Co., China) at 554 nm (293 nm).

3. Results and discussion

3.1. Characterization of the WO₃/W cathode

Fig. 1. SEM images (a–e) and EDX (f) analysis of the WO_3/W cathode under different magnifications.

Fig. 1. depicts the self-assembled WO_3 nanoparticles formed on the surface after the calcination and oxidation treatment of the tungsten wire. The nanoparticles structure is advantageous for the larger surface area for both charge transfer and catalyst-electrolyte interfacial contact. This method of cathode preparation is easy. As shown in the energy dispersive X-Ray spectroscopy (EDX) image (Fig. 1(f)), the main elements on the tungsten wire were tungsten and oxygen. From the ratio of the atoms, the product was WO_3 .

To measure the reduction performance of WO_3/W for NO_3^- -N, the CV curves of the WO_3/W cathode were compared in different electrolytes (100 mg/L NO_3^- -N + 0.05 mol/L FA, 0.05 mol/L Na_2SO_4) with UV (Fig. 2(a)) and without light (Fig. 2(b)). N_2 was bubbled into the electrolyte for 30 min to remove O_2 . There was no redox peak when the electrolyte was Na_2SO_4 . However, a reduction peak was observed when the electrolyte

was NO_3^- -N and FA. This demonstrated that the WO_3/W cathode reduced NO_3^- -N in the cathode chamber. When no light was irradiated on the WO_3/W , the current was a little lower than with the UV light. The reduction peak was significant because it showed that a cathodic reduction reaction occurred with NO_3^- -N when without light. UV irradiation was beneficial for e^- generation and increased the current intensity. This made the NO_3^- -N reduction reaction easier. However, this will increase the energy consumption. Consequently, NO_3^- -N was reduced in the self-biased internal electric field system without light.

3.2. *I-t* curves of the electrodes

I-t curves of the two electrodes in Na_2SO_4 solution (0.2 mol/L) at zero external bias were collected to investigate their

Fig. 2. CV curves of the WO_3/W cathode in different electrolytes (100 mg/L NO_3^- -N + 0.05 mol/L FA, 0.05 mol/L Na_2SO_4) with UV (a) and without light (b).

Fig. 3. *I-t* curves recorded with no external bias in 0.2 mol/L Na_2SO_4 and without light.

performance in the dark. Cells based on $\text{TiO}_2/\text{g-C}_3\text{N}_4$ anode and Pt cathode, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ anode and WO_3/W cathode, WO_3/W anode and Pt cathode were used for the tests. WO_3 cannot generate electrons due to its relative positive conduction band (CB) level [25]. The $\text{WO}_3/\text{W-Pt}$ cell showed negligible performance, with the nearly zero current in the dark indicating that the system based on WO_3/W anode was not useful for electron generation (Fig. 3). $\text{TiO}_2/\text{g-C}_3\text{N}_4\text{-Pt}$ ($\sim 15 \text{ mA/cm}^2$) can generate more electrons than $\text{WO}_3/\text{W-Pt}$ ($\sim 0.005 \text{ mA/cm}^2$), $\text{TiO}_2/\text{g-C}_3\text{N}_4\text{-WO}_3/\text{W}$ ($\sim 0.09 \text{ mA/cm}^2$) and even $\text{TiO}_2/\text{g-C}_3\text{N}_4$ microspheres ($\sim 0.03 \text{ mA/cm}^2$) [31,33] with light irradiation and an applied voltage (0.5 V). Meanwhile, the holes generated in TiO_2 can perform RhB or TCS oxidation due to its positively located valence band (VB) edge. For more electrons to be transferred from the anode to the cathode, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ was used as the anode and WO_3/W was the cathode.

To study the influence of aeration, *I-t* curves were recorded with no external bias. $\text{TiO}_2/\text{g-C}_3\text{N}_4$ was used as the anode, platinum sheet as the counter electrode, and a saturated calomel electrode as the reference electrode in the different electrolytes (0.05 mol/L NaOH + 10 mg/L RhB, 0.05 mol/L NaOH + 50 mg/L TCS) without light. When the system was not aerated, most electrons moved from the heterojunction to the cathode, and the current was larger. As shown in Fig. 4(a) and (b), the cur-

rent decreased when the electrolyte with pollutants was aerated. This was caused by the consumption of the electrons on $\text{TiO}_2/\text{g-C}_3\text{N}_4$ for activating O_2 and generating ROS. EPR data showed that electrons generate from the anode activated O_2 and formed ROS in the dark [24]. Thereby, the electrons transferred from the anode to cathode were reduced and the current was decreased. Similarly, WO_3/W was used as the anode, with platinum sheet as the counter electrode and a saturated calomel electrode as the reference electrode, in 0.05 mol/L FA + 100 mg/L NO_3^- -N without light (Fig. 4(c)). After bubbling N_2 to remove O_2 in the electrolyte, the electrons generated from WO_3/W was used for NO_3^- -N reduction directly and few electrons moved from WO_3/W to the Pt cathode.

In contrast, when the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ anode and WO_3/W cathode were placed in the two electrode chambers, where the anode chamber with filled with 0.05 mol/L NaOH + 10 mg/L RhB and the cathode chamber with 0.05 mol/L FA + 100 mg/L NO_3^- -N. Simultaneously, the anode chamber was aerated with air and the cathode chamber was bubbled with N_2 . The *I-t* curves (Fig. 5(a)) showed that the current was larger than without aeration with air and N_2 . Likewise, a similar result was observed when 10 mg/L RhB was used instead of 50 mg/L TCS (Fig. 5(b)). This manifested that it was beneficial for electron generation and transfer. This system facilitated pollutant degradation and electron generation.

3.3. Self-based tiny current for RhB (or TCS) and NO_3^- -N degradation

Compared to the traditional method, the method here can oxidize anodic pollutants and reduce cathodic contaminants without light irradiation or an externally applied voltage. A 1000 Ω external resistance was placed between the anode and cathode. This system removed $\sim 90\%$ RhB and reduced $\sim 95\%$ NO_3^- -N (Fig. 6(a)) under UV light after 4 h, and generated photo-excited electrons (Fig. 6(b)). Interestingly, it could also remove $\sim 75\%$ RhB and $\sim 82\%$ NO_3^- -N with the self-biased tiny current without any light (Fig. 6(a)). Upon oxidation of RhB by ROS, some electrons were generated, which may in part compensate for the consumption of electrons by O_2 activation. The current decreased with the decrease of pollutant concentration.

Fig. 4. *I-t* curves recorded with no external voltage and light in 0.05 mol/L NaOH + 10 mg/L RhB ((a), aeration, $\text{TiO}_2/\text{g-C}_3\text{N}_4\text{-Pt}$), 0.05 mol/L NaOH + 50 mg/L TCS ((b), aeration, $\text{TiO}_2/\text{g-C}_3\text{N}_4\text{-Pt}$), and 0.05 mol/L FA + 100 mg/L NO_3^- -N ((c), N_2 , $\text{WO}_3/\text{W-Pt}$).

Fig. 5. *I-t* curves of TiO₂/g-C₃N₄ (aeration) and WO₃/W (N₂) in two chamber at zero external and without light.

Fig. 6. RhB and NO₃⁻-N degradation rate in the anode and cathode chamber (a) and the spontaneous current (b) in the system with and without light.

To investigate the degradation efficiency for other pollutants such as antibiotics, TCS was used to replace RhB in the anode chamber. Along with the generation of photo-excited electrons (Fig. 7(b)), ~98% triclosan was degraded and ~81% NO₃⁻-N in the cathode chamber was removed in 60 min (under UV light). When visible light was irradiated instead of UV light, ~94% triclosan was degraded and ~80% NO₃⁻-N was removed. Although both the decomposition/degradation efficiency and

current intensity without light were lower than with UV light, ~92% triclosan and ~78% NO₃⁻-N were degraded in the self-biased system under the internal electric field.

3.4. Degradation mechanism

The CB of the TiO₂ and g-C₃N₄ anodes is more negative than that of the WO₃/W cathode. Similar to the build-up of an inter-

Fig. 7. TCS and NO₃⁻-N degradation rate in the anode and cathode chamber (a) and the spontaneous current (b) in the system with and without light.

Fig. 8. Degradation mechanism of the self-sustained system.

nal electric field between the heterojunctions $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and WO_3/W , the potential difference (or Fermi Level difference) between the more positive WO_3/W and more negative $\text{TiO}_2/\text{g-C}_3\text{N}_4$ thus built a self-biased internal electric field. This caused electrons to migrate from the anodic $\text{TiO}_2/\text{g-C}_3\text{N}_4$ to the WO_3/W cathode, which facilitated electron/hole pair separation on the two electrodes. That is, spontaneous electron transfer between the two electrodes occurred. Therefore, this system does not require an external bias to drive activation, oxidation of organics at anode and reduction of nitrate at cathode.

At the anode, because the CB of $\text{g-C}_3\text{N}_4$ (-1.12 V vs. NHE) is more negative than the reduction potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.28 V vs. NHE), so e^- on the CB of $\text{g-C}_3\text{N}_4$ can effectively activate O_2 and generated $\cdot\text{O}_2^-$. We have reported that the e^- of the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ anode can activate O_2 and generate ROS under light illumination and without light [24].

As shown in Fig. 8, RhB (or TCS) in the anode chamber and NO_3^- -N in the cathode chamber were removed simultaneously. By accepting e^- , O_2 can be activated on $\text{g-C}_3\text{N}_4$ (e^-) and TiO_2 (e^-) to produce $\cdot\text{O}_2^-$ via a one-electron reduction process. $\cdot\text{O}_2^-$ is a ROS that can decompose organic pollutants (RhB, TCS) into small molecules, even to CO_2 and H_2O . Furthermore, $\cdot\text{O}_2^-$ can be reduced to $\cdot\text{OH}$ via the two-electron reduction process. In addition, the electrons of the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ anode transferred to the WO_3/W cathode can reduce NO_3^- -N, while the h^+ on $\text{TiO}_2/\text{g-C}_3\text{N}_4$ with a high oxidation power can decompose the organic pollutants (RhB, TCS). After pollutant degradation, some electrons were also generated in this system. By utilizing the spontaneous tiny current, simultaneously, two kinds of pollutants in wastewater were treated and removed at the anode and cathode chamber without light illumination.

4. Conclusions

A self-biased internal electric field system with a highly efficient $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction anode and WO_3/W cathode for pollutant degradation was reported. The WO_3/W cathode nano-catalyst was readily prepared by heating and oxidation of

a tungsten wire in air, and was studied by SEM or CV. This self-sustained catalytic fuel cell system oxidized RhB and TCS and reduced NO_3^- -N, simultaneously. The degradation mechanism was discussed. The CB of $\text{g-C}_3\text{N}_4$ is more negative than TiO_2 , and TiO_2 is more negative than WO_3 , and an interior bias was produced to cause the transfer of e^- from $\text{g-C}_3\text{N}_4$ and/or TiO_2 to WO_3 through an external circuit. The anodic $\text{TiO}_2/\text{g-C}_3\text{N}_4$ catalytic reactor system can generate spontaneously a tiny current and activate O_2 without light irradiation. The anodic catalyst was conducive to the separation of photo-generated e^-/h^+ pairs and e^- transfer to the cathode without light. The potential of this low energy consumption system was highlighted for degrading and removing different pollutants by novel self-biased assemblies.

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Graphical Abstract

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Dalian University of Technology

Without light or externally applied voltage, a new self-sustained catalytic fuel cell with anodic $\text{TiO}_2/\text{g-C}_3\text{N}_4$ catalyst and cathodic WO_3/W nano-catalysts was established and generated spontaneous current. It can oxidize and reduce different pollutants simultaneously.

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阳极 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 与阴极 WO_3/W 纳米催化剂之间扩大的异质结 自偏压系统去除污染物

于婷婷^a, 柳丽芬^{a,b,*}, 杨凤林^a^a大连理工大学环境学院工业生态与环境工程教育部重点实验室, 辽宁大连116024^b大连理工大学食品与环境学院, 辽宁盘锦124221

摘要: 电化学或光电化学半导体催化剂广泛应用于降解污水中的有机与无机污染物, 有望实现低能耗且高效的污染物降解。目前, 已有多种异质结半导体光催化剂的研究报道, 并且大多数的研究结果显示催化剂活性有明显提高, 但仍存在着光激发后电子与空穴的复合问题。光电化学系统的构建可减少电子与空穴的复合, 因光催化阳极与光催化阴极之间费米能级的不同, 在两极之间形成异质结, 产生内电场, 自生偏压驱动电子流动。已有诸多研究报道将 TiO_2 催化剂与 $\text{g-C}_3\text{N}_4$ 复合

形成异质结, 提高光催化活性. 由于 $\text{g-C}_3\text{N}_4$ ($\sim -1.12 \text{ eV vs. NHE}$) 导带位置相比于 TiO_2 ($\sim -0.2 \text{ eV vs. NHE}$) 更负, 因此在两者之间可形成内部偏压, 驱动电子由 $\text{g-C}_3\text{N}_4$ 转移至 TiO_2 . WO_3/W 导带位置 ($\sim +0.2 \text{ eV vs. NHE}$) 比 TiO_2 与 $\text{g-C}_3\text{N}_4$ 更正, 因此自生内偏压促进电子由阳极流动至阴极.

我们研究组发展了一种在无光条件下的自偏压电化学燃料电池系统, 异质结间的电子流动可活化氧气产生自由基, 自由基可用于阳极污染物的降解, 但阴极未降解污染物. 本文在上述研究基础上, 应用 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 异质结与 WO_3/W 分别作为阳极与阴极催化剂, 构建自偏压催化燃料电池系统, 在无光条件下催化阳极与阴极之间自发电子转移, 活化氧气产生自由基, 同时实现低能耗阳极室内污染物如罗丹明B和三氯生的氧化, 且电子用于阴极室内硝态氮的还原.

通过在空气中原位加热与氧化钨丝制得 WO_3/W 阴极, 由扫描电镜图可知在钨丝表面形成三氧化钨纳米粒子, 此结构增大了催化剂的表面积以及催化剂与电解液的接触面积, 有利于电荷转移. 用循环伏安曲线(CV)与电流时间曲线($I-t$)表征了电极的电化学性质. CV测试结果表明, 相比于硫酸钠电解液, WO_3/W 阴极在含有硝态氮的电解液中存在还原峰, 且紫外照射比无光条件下的电流略大, 说明此电极在无光条件下可用于还原硝态氮, 有光更利于激发催化剂产生电子与空穴降解和去除污染物. 在硫酸钠电解液中, 无光照条件下(同室), $I-t$ 曲线表明 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 相比于 WO_3/W 电极可产生更大电流, 因此选择 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 作为阳极, WO_3/W 作为阴极. 在含污染物电解液中, 无光照条件下, Pt片作为对电极时(同室), $I-t$ 曲线中的电流在曝气时比未曝气时小, 说明电极上产生的部分电子用于活化氧气产生自由基, 因此转移到外电路的电子减少, 电流变小; 相反, 当 $\text{TiO}_2/\text{g-C}_3\text{N}_4$ 阳极置于阳极室, WO_3/W 阴极置于阴极室时(两室), 阳极鼓入空气, 阴极曝氮气时, 电流比两室均未曝气时大, 说明此系统有利于电子产生与转移, 用于氧化还原去除污染物. 相比于传统方法, 此系统通过阳极室内曝空气与活化分子氧形成自由基, 无需外加偏压, 在有光与无光条件下, 均可实现对阳极室与阴极室内不同污染物的同时去除或降解, 同时提出了此系统中的降解机理.

关键词: 自偏压系统; 异质结; 无光照; 低能耗; 污染物降解

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*通讯联系人. 电话: (0427)2631799; 传真: (0411)84708084; 电子信箱: lifenliu@dlut.edu.cn

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