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A novel anode with anticorrosive coating for efficient degradation of toluene

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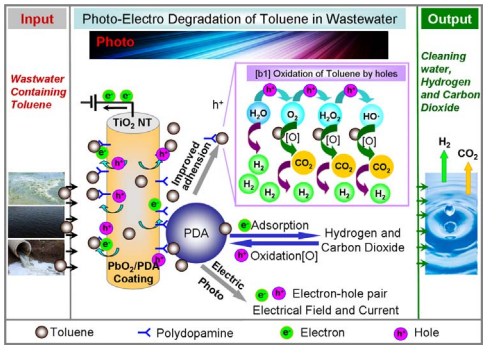
GRAPHICAL ABSTRACT



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ABSTRACT

The polydopamine (PDA) coating was used to modify the surface of the PbO_2/TiO_2 nanotube arrays (PTNAs) by impregnation method. The obtained PDA-PbO_2/TiO_2 nanotube arrays (PPTNAs) coating exhibited a sandwich structure and used as anode for photoelectrochemical degradation of toluene. Generally, due to the symmetric structure and conjugation of methyl with benzene ring, the degradation of toluene was difficult to carry on. Our results show that the rate of toluene degradation can reach up to 66% at the surface of PPTNAs coating anode, it is much higher than that of the TiO_2 nanotube arrays coating anode, 17%. The reduction product at cathode, hydrogen, was also measured, which is one of the valuable source of energy. In the coupled effect of applied voltage and photocatalysis on the PPTNAs anode, the degradation of toluene was carried out smoothly. The introduction of lead dioxide nanoparticles on the coated anode possessed favorable electronic conductivity in strong acid, which is benefit for a high rate of electrons transportation at the interface of TiO_2 and lead dioxide. The excellent corrosion resistance of PPTNAs coating further ensured the effective degradation of toluene with long-term stability. Meanwhile, the unique adhesion of the outer PDA coating increased the contact opportunities between toluene molecules and the anode surface, and enhanced the photocatalytic activity of the PPTNAs coating anode. The applied voltage suppressed the recombination of electron-hole pairs and provided abundant reaction sites. All of these increased the photo-electro catalysis of toluene degradation. The new fabricated anode material shows good prospective application of cleaning up refractory pollutants and the resource utilization.

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1. Introduction

Followed the development of energy science and environmental protection, the utilization of efficient solar energy and advanced electrode materials has attracted widespread attentions [1]. One of the most promising methods of solar energy conversion is artificial photochemistry for synthesis, degradation, or reactions in biological pathways [2]. Up to now, due to the lack of best materials, the direct use of solar energy for renewable energy production and pollutant treatment remains a fascinating challenge. Among various materials for efficient utilization of solar energy, TiO_2 has stood out from other photocatalysts due to its low cost, stable property as well as high photocatalytic activity even in rigorous environments. The pioneering works of Fujishima have proved that the TiO_2 could be used as a photoelectrode to electrochemical photolysis of water [3]. In recent years, extensive researches on performance improvement of TiO_2-based photoelectrodes have been carried out.

TiO_2 nanotube arrays (TNAs), having the inherent advantage of directionality, have attracted continuous interest in many fields of science and technology for large specific surface area, higher adsorption capacity and the excellent photocatalytic activity. TNAs have been widely used as electrode material and catalyst in solar cell, photocatalyst, and bioactive surface coating. However, the TNAs still share the intrinsic defects of TiO_2, such as unable to use the visible light part of the solar energy for its wide band gap and the recombination of photogenerated electron-hole pairs, when they were used as the photoelectrode. The good news in recent years is, scientific researches show that the modification of TiO_2 nanomaterials could harvest visible light and improve the spatial separation of charges efficiently [4].

Nowadays, many doping methods can be devoted to modify the surface of titanium dioxide, such as the transition metal (Ag, Pt, Ca) [5–7], the non-metal (N, F, S, C) [8–11] and the metal oxide (RuO_2, Co_3O_4, ZrO_2) [12–14] doped TiO_2. There is a synergistic effect between TiO_2 and dopants in the photochemical reaction, which provides a promoting effect for the active components and carriers.

Due to the chemical stability, good conductivity and inexpensive, lead dioxide (PbO_2) has become an important oxide that can be used in fundamental and applied electrochemistry. Reports showed that the outstanding electrical conductivity of PbO_2 makes it behaving as a metal in the electrochemical reactions [15]. PbO_2 is widely used as anode owing to large overpotential for oxygen evolution and the production of hydroxyl radicals that followed the water electrolysis. Up to now, PbO_2 becomes one of the best choices of anode material for the degradation of organics [16]. In generally, lead (Pb) used as electrode has shortcoming for releasing toxic ions, especially in the acid solution. On the contrary, PbO_2 electrode shows strong stability and reactivity in acidic conditions during electrochemical reaction [17]. In addition, PbO_2 is capable of depositing on metal matrix such as Ti, Au, and Pt to improve the mechanical strength and reactivity, especially PbO_2 has good adhesion to the titanium substrate. However, there still exists the problem of corrosion during the electrochemical reaction for PbO_2/Ti electrode. Therefore, it is urgent to seek an effective solution to fabricate a novel anode with anticorrosion and high efficiency of catalysis.

As a kind of mussel protein, dopamine (DA) can be oxidized and spontaneously self-polymerize to polydopamine (PDA). PDA incorporates many functional groups such as catechol, amine, and imine those make it displaying many striking properties in optics, electricity, and bioadhesive [18,19]. Therefore, PDA has been rapidly incorporated into a wide range of applications across the chemical, medical, material science, especially as a functional coating and anticorrosion material. The most exciting findings have been achieved in recent years that PDA possesses unique photosensitivity and desirable application in the area of electrocatalysis [20].

With the increasing shortage of water resource, and evolutionary serious situation of water pollution, the urgent duty and challenge is that a large amount of organic matters exist in the wastewater and difficult to be removed completely. Refractory organic, mono-aromatic hydrocarbon such as benzene, toluene and xylene is known to be toxic, hard to be degraded and having trends to pollute water seriously. And so far, many methods are not effective in dealing with such organic pollutants. Among those water treatment methods against the pollution of organics, electrochemical degradation is one of the most prospective ways. However, there are few studies on the electrochemical treatment of refractory aromatic organic pollutants which are very difficult to degrade. The electrochemical oxidation of toluene has been studied [21], and results show that the electrocatalytic activity and stability of the electrode material will affect both the process selectivity and reaction efficiency. It is expected that a novel anode material with high over-potential of oxygen evolution, and high rate of the complete degradation of toluene to CO_2 could be obtained. The PbO_2/TiO_2 composite is an appropriate option of anode material for the treatment of toluene in wastewater.

As we know, wastewater treatment often occurs in an acid environment, the corrosion of electrode by electrochemical method should be solved effectively. Therefore, in this paper, the PDA was introduced to enhance the adhesion and corrosion resistance of the PbO_2/TiO_2 nanotube arrays (PTNAs), the addition of PbO_2 will enhance the electric conductivity of TiO_2 anode for the PbO_2 behaves as a metal in the electrochemical reactions of acid medium, and TiO_2 substrate has been selected for its UV sensitivity and high reactivity in acid solution. The PDA-PbO_2/TiO_2 nanotube arrays (PPTNAs) coating material was utilized as the new anode for toluene degradation under the coupling of applied voltage and light irradiation. With the synergistic of applied voltage and photo irradiation (UV and visible light), the PPTNAs coating anode showed corrosion resistance in acid solution, and a high degradation rate of toluene was achieved. Mechanisms of the photoelectrochemical degradation of toluene at the anticorrosive PPTNAs coating anode are explored, and the corresponding synergistic effect of applied voltage and photocatalysis for wastewater treatment was further discussed.

2. Experimental section

2.1. Materials

Titanium (99.6%, 2 mm thick) was purchased from Sigma-Aldrich. Ethylene glycol ($(CH_2OH)_2$), ammonium fluoride (NH_4F), nitric acid (HNO_3), surfactant (sodium dodecyl benzene sulfonate, $C_{18}H_{29}NaO_3S$, SDBS) and sulphuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Lead nitrate ($Pb(NO_3)_2$, AR, 99.5%) were purchased from Shiyi Chemical Reagent Co., Ltd (Shanghai, China). Dopamine and tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl) were supplied from Tianke Trade Co., Ltd (Suzhou, China). All aqueous solutions were prepared with high purity water by a Millipore Milli-Q system at 25 °C, all AR grade and used as received; deionized (DI) water was HPLC grade.

2.2. Preparation of the anatase TNAs

Titanium sample was cut into pieces of $20 \times 10\,mm^2$, it was first degreased by sonicating in acetone, ethanol and room-temperature deionized water for 15 min respectively. In the anodization process, a conventional two-electrode system with the Ti sheet as an anode and a Pt gauze (Aida, 52 mesh) as a cathode has been carried out. All electrolytes consisted of 0.2 g NH_4F, 1.2 mL deionized water and 60.0 mL glycol. The Ti sheet was anodized at 50.0 V for 30 min, and a layer of TNAs film generates on the surface of the Ti substrate. After the anodization, the prepared TiO_2 nanotube arrays sample was cleaned with DI water. The anodized TNAs were annealed at 450 °C in oven for 3.0 h with a heating rate of 10 °C/min, then the anatase TNAs film has been fabricated. All anode materials were carried out at room temperature.