Photoelectrocatalytic degradation of organic contaminants at Bi₂O₃/TiO₂ nanotube array electrode

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ABSTRACT

In the current work, TiO₂ nanotube array was prepared via electrochemical anode method. Then the Bi₂O₃ nanoparticles were deposited onto the TiO₂ nanotube array via dip-coating method from an amorphous complex precursor. The crystal structures were characterized via X-ray diffraction analysis. Their surface textures were observed via electron-scanning microscope. The prepared composite array electrode exhibited high photoelectrocatalytic activities towards degrading organic contaminants under visible light irradiation. High photoelectrocatalytic activities were also exhibited under UV light irradiation. The catalytic mechanism was discussed based on the analysis of electrochemical and degradation kinetics results. It is suggested a P (Bi₂O₃)-N (TiO₂) junction was formed to increase the catalytic activities. The stability of the electrode materials was confirmed finally.

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1. Introduction

In recent years, highly ordered TiO₂ nanotube arrays prepared by electrochemical anodization have attracted much attention due to their unique architecture. A TiO₂ nanotube array can form a uniform TiO₂ film on a titanium substrate, which provides an ordered structure and porous surface, without a decrease in geometric thickness [1]. Such an infrastructure is especially favorable for mass diffusion. Therefore, TiO₂ nanotube arrays show great potential for practical environmental purification [2,3].

As a wide band gap semiconductor, TiO₂ need to be excited by an ultraviolet light which is less than 5% of the solar irradiance at the Earth's surface. To prepare TiO₂ photocatalysts with visible light responsibility, several strategies have been adopted. One of the approaches is coupling TiO₂ with other semiconductor with appropriate band gaps. A large number of coupled polycrystalline or colloidal semiconductor, in which the particles adhere to each other in so-called sandwich structures or present a core-shell geometry, have been prepared such as SiO₂-TiO₂, CdS-TiO₂, ZnO-TiO₂, SnO₂-TiO₂, NiO-Bi₂O₃, etc. Recently, several coupled systems such as Bi₂O₃/SiTiO₃ [4–7] were reported to be efficient under visible light irradiation. However, the photocatalytic mechanism for the coupled system has not been systematically investigated, and no clear evidence was provided for the complete decomposition of organic pollutants under visible light.

Bismuth oxide, Bi₂O₃, due to its high refractive index, dielectric permittivity, marked photoconductivity and photoluminescence, is used in a variety of areas, such as sensor technology, optical coatings, and electrochromic materials. As a photocatalyst, Bi₂O₃ is a p-type semiconductor with conduction and valence band edges of +0.33 and +3.13 V (vs. NHE), respectively [8]. Under visible light irradiation, the photogenerated electron and hole is able to oxidize water. And, highly reactive species, such as O₂•⁻ and •OH radicals may be generated, which may act as initiators of oxidation reactions [8–10].

In the present paper, we report a novel loading of Bi₂O₃ nanoparticles onto a TiO₂ electrode with a highly ordered vertically oriented nanotube array prepared by anode oxidation. The obtained results indicated that organic contaminants can be efficiently degraded by the Bi₂O₃/TiO₂ nanotube array electrode under UV and visible light irradiation. And, the composite electrode exhibited higher catalytic activities towards the degradation of organic contaminants than the individual Bi₂O₃ or TiO₂ electrode did. The enhanced mechanism was discussed. 2,4-Dichlorophenol, a kind of typical refractory contaminants was used in the present work.

2. Experimental

2.1. Preparation and characterization of Bi₂O₃/TiO₂ nanotube array

All chemicals were analytical grade reagents and used without further treatment. Electrolyte was freshly prepared from deionized

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Fig. 1. (a) The XRD patterns for TiO_2 (A) and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ (B) nanotube composite array electrodes, (b) SEM analysis of TiO_2 (A) and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ (B) nanotube composite array electrodes.

water. After chemical polishing, titanium foil (thickness about $250\ \mu\text{m}$, purity 99.4%, Beijing Cuibolin Non-Ferrous Technology Developing Co., Ltd.) was subjected to potentiostatic anodization in an electrochemical anodization cell with a platinum cathode in a 0.5 wt% HF + 1 M H_3PO_4 electrolyte at ambient temperature. The potential of 20 V was applied for 30 min. Then the samples were rinsed with deionized water and annealed at 450°C for 24 h. Porous Bi_2O_3 nanoparticles were deposited onto the TiO_2 nanotube array from an amorphous heteronuclear complex via a dip-coating method.

X-ray diffraction (XRD) of the composite electrodes was recorded on a Scintag-XDS-2000 diffractometer with $\text{Cu K}\alpha$ radiation. The morphology of the Bi_2O_3 nanoparticles was characterized by a JSM 6301 electron-scanning microscope (SEM). The photoelectrochemical measure employed a basic electrochemical system (Princeton Applied Research) connected with a counter-electrode (Pt wire, 70 mm in length with a 0.4-mm diameter), a working electrode (the hybrid electrode, active area of $11\ \text{cm}^2$), and a reference electrode (a saturated calomel electrode (SCE)). Na_2SO_4 solution (0.12 mg/L) was used as electrolyte solution.

2.2. Degradation experiments

Degradation experiments were performed in a cylindrical quartz reactor. The reactor, which contained a 60 mL sample solution allowing 4.5 cm of the supported film electrode to be immersed

into the solution, was placed 3 cm in front of a 150 W Xe lamp purchased from the German Osram. The intensity of light, as measured by an irradiance meter (Instruments of Beijing Normal University) was c.a. $25\ \text{mW}/\text{cm}^2$ at 4 cm into the reactor, the position where the electrode was placed. The photoelectrocatalytic (PEC) reaction employed a basic electrochemical system (Princeton Applied Research) connected with a counter-electrode (Pt wire, 70 mm in length with a 0.4-mm diameter), a working electrode (hybrid electrode, active area of $10\ \text{cm}^2$), and a reference electrode (a saturated calomel electrode (SCE)). 0.1 M Na_2SO_4 solution was used as electrolyte solution. Initial concentration of the organic contaminants solution was 10 mg/L and was analyzed by reversed-phase high performance liquid chromatogram (HPLC) with a Hitachi HPLC apparatus (Diode Array Detector L-2450, Column Oven L-2300, and Pump L-2130). All experiments were carried out at least in duplicate. The reported values are within the experimental error of $\pm 3\%$.

3. Results and discussion

3.1. Characterization of the composite film electrode

The XRD patterns revealed that all the undoped TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ samples displayed well-crystallized anatase phase after being calcined at 773 K (Fig. 1(a)). The Bi-species are present in a separated phase of Bi_2O_3 . The peak at 27.42° is identified as the main peak of $\alpha\text{-Bi}_2\text{O}_3$ with cubic phase. The typical SEM images

Fig. 2. Effects of applied bias potentials and light irradiation on EIS variation at TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanotube array electrodes (0.1 M Na_2SO_4).

of TiO_2 nanotube and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanotube composite samples are shown in Fig. 1(b). It is clear that TiO_2 nanotube is successfully fabricated by anodic oxidation and most of the nanotubes are uniform in size and highly oriented. Interestingly, tubular structures are still in existence after Bi_2O_3 deposition (Fig. 1(b)). However, the morphology of composite nanotube composite is different from that of TiO_2 nanotube. These Bi_2O_3 nanoparticles are deposited on the top of TiO_2 nanotube or entered into tube.

3.2. Photoelectrochemical properties

Electrochemical impedance spectroscopy (EIS) is an effective tool for probing the features of surface-modified electrodes and was further employed to analyze the semiconducting properties of the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanotube array electrodes. As shown in Fig. 2, both samples show a pronounced arc (semicircle portion) at higher frequencies in the EIS plane, whose diameter corresponds to the electron-transfer resistance controlling the kinetics at the electrode interface. Significant changes in the EIS spectra are observed for the composite electrodes, following Bi_2O_3 modification. In fact, deposition of the Bi_2O_3 nanoparticles on the TiO_2 nanotube electrode results in a marked decrease of semicircle diameter, which justifies an analogous decrease of the electron-transfer resistance and relates directly to the accessibility of the underlying electrode or the film permeability. In this case, the enhanced performance of the composite TiO_2 nanotube electrode could originate from the improvement of charge carrier separation.

Fig. 3. LSV analysis of TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanotube array electrodes with and without Xe lamp or visible light irradiation ($\lambda > 400$ nm) (0.1 M Na_2SO_4).

At the meantime, current response of TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ electrode with light irradiation and without light irradiation was observed (Fig. 3). It can be observed that under Xe lamp irradiation, the TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ electrodes exhibited enhanced current response compared with that under dark condition. And, it is observed that no photocurrent was observed under visible light irradiation for TiO_2 electrode. By contrast, photocurrent was observed for $\text{Bi}_2\text{O}_3/\text{TiO}_2$ electrode under visible light irradiation. It is concluded that it is the Bi_2O_3 nanoparticles that contribute to the generation of photocurrent under visible light irradiation.

3.3. Degradation of organic contaminants

Under UV and visible light irradiation, degradations of target organic contaminants were performed in the processes of individual electrolysis (1.5 V), individual photocatalysis, and photoelectrocatalysis process. Under visible light irradiation, as shown in Fig. 4(a), organic contaminants can be photocatalytically degraded using the composite film electrode; it can also be degraded via the electro-oxidation process at the bias potential of 1.5 V. Clearly, the degradation rate of organic contaminants was the highest under the PEC process with the same bias potential. Thus, it can be concluded that a sort of synergetic effect occurs during the PEC process in the degradation of organic contaminants. Additionally, no concentration variation was observed in the presence of the film electrode without visible light irradiation. Thus, it was concluded that the

Fig. 4. Removal efficiency of target pollutants in PEC, PC, and EC processes with visible light or UV light irradiation.

adsorption effect can be ignored within the reaction process. Similar results were observed under UV light irradiation. As shown in Fig. 4(b), the target contaminants can be degraded via photocatalysis process and electrolysis, respectively. And, the degradation rate of target contaminants was largely improved with PEC process with the same light irradiation and applied bias potential.

3.4. Mechanism analysis

It has been reported that the TiO_2 is a potential photocatalyst in decomposing organic contaminants under UV light irradiation. Thus, it is considered that TiO_2 works as a main photocatalyst for the $\text{Bi}_2\text{O}_3/\text{TiO}_2$, while the role of Bi_2O_3 is a sensitizer absorbing visible light. It is reported that the VB of Bi_2O_3 is lower by 0.7 V than that of TiO_2 [11]. Under visible light irradiation, the electrons in the VB of Bi_2O_3 are excited to its CB. Therefore, the VB of Bi_2O_3 is ren-

dered partially vacant, and the electrons in the VB of TiO_2 can be transferred to that of Bi_2O_3 . As a result, holes are generated in the VB of TiO_2 . These above processes initiate photocatalytic oxidation reactions. Therefore, with the irradiation of visible light, the heterojunction system can induce efficient degradation of organics. In the heterojunction prepared in this study, the Bi_2O_3 and TiO_2 nanotube are tightly bound each other in nanosized level. Therefore, the hole transfer through the junction will be greatly efficient. Moreover, the TiO_2 working as main photocatalysts is uncoated completely by the Bi_2O_3 nanoparticles. Thus the effective catalytic sites are not screened by the formation of heterojunction structure.

As the band gap of Bi_2O_3 is ca. 2.85 eV, it can be excited by light with wavelength less than 435 nm. Due to the high electron-hole recombination rate in Bi_2O_3 , the photocatalytic activity of Bi_2O_3 is very low. Because the valence band of Bi_2O_3 is lower than that of titanium oxide [12], the heterojunctions formed in the composite nanotube film will promote the photogenerated holes in Bi_2O_3 to be transferred to the upperlying valence bands of titanium oxide. Thus, the photocatalytic activity of the composite electrode was enhanced.

4. Conclusions

The Bi_2O_3 nanoparticles was partly deposited onto self-organized TiO_2 nanotube arrays from amorphous complex via dip-coating method. It has been demonstrated the surface functionalization by coated Bi_2O_3 nanoparticles, providing a composite vertically oriented nanostructure and exhibited high photoelectrocatalytic activities towards the degradation of organic contaminants under UV and visible light irradiation.

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