Materials Science in Semiconductor Processing 85 (2018) 150–159

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Synthesis of tin and molybdenum co-doped TiO_2 nanotube arrays for the photoelectrocatalytic oxidation of phenol in aqueous solution

Xiaoyue Ma[a], Zhirong Sun[a,*], Xiang Hu[b,*]

[a] National Engineering Laboratory for Advanced Municipal Wastewater Treatment and Reuse Technology, Beijing University of Technology, Beijing 100124, PR China
[b] College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Keywords:
Nanotube arrays
Co-doping
Anodization
Photoelectrocatalysis
Oxidation
Phenol

ABSTRACT

Tin and molybdenum co-doped titanium dioxide nanotube arrays was prepared by single-step anodization of titanium plate (Sn-Mo-TiO_2 NTs/Ti electrode). The Sn-Mo-TiO_2 NTs/Ti electrode was characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The length and inner diameter of nanotubes increased with the increase of anodization voltage. The influences of factors, such as anodization voltage, anodization time, concentrations of Sn^{4+} and Mo^{6+}, and calcination temperature, on the preparation of the electrode were studied by chronoamperometry under simulated sunlight irradiation. The optical performance of Sn-Mo-TiO_2 NTs/Ti electrode was tested by UV–vis spectrophotometer. Sn-Mo-TiO_2 NTs/Ti electrode exhibited high adsorption in the visible region relative to pure titanium dioxide nanotube arrays. Additionally, the chronoamperometry test results highlighted that the doping of tin and molybdenum could enhance the photoelectrochemical performance of the electrode. The electrode exhibited good photoelectrocatalytic oxidation capacity on phenol at 0.5 V constant bias voltage. Applied bias voltage enhanced the photocatalytic efficiency of nanotube arrays via promoting the separation of photogenerated electron-hole pairs. A possible degradation process for phenol was proposed.

1. Introduction

Photoelectrocatalysis is a composite technology which combines photochemistry and electrochemistry. It has been used for oxidation degradation of organics and hydrogen production from water [1–3]. Under the external electric field, the photogenerated electrons on photoelectrode transfer to the counter electrode, which reduces the recombination of photogenerated electron-hole pairs on photoelectrode significantly and improves the photocatalytic performance [4].

Titanium dioxide (TiO_2) is widely used as photocatalytic material owing to its nontoxicity, hydrophilicity, low price, high oxidation ability and chemical stability [5–7]. Under the ultraviolet (UV) light irradiation, electrons in the valence band are excited and jump to the conduction band of TiO_2, generating photogenerated electron-hole pairs. Photogenerated electrons in the conduction band are captured by O_2 to generate superoxide radical ions ($\cdot O_2^-$), while photogenerated holes in the valence band oxidize hydroxyl (OH^-) and H_2O to hydroxyl radicals (·OH) [8,9]. Superoxide radical ions and hydroxyl radicals can degrade organic compounds effectively because of their strong oxidizing properties.

However, two defects of TiO_2 limits its application: the poor absorbance of visible light due to the wide band gap of TiO_2 (rutile, ~3.0 eV; anatase, ~3.2 eV), and the low quantum efficiency because of the higher recombination rate of photogenerated electrons and holes. Therefore, numerous methods have been investigated to shift the absorption spectrum of TiO_2 from the UV into the visible light range and to improve the separation of photogenerated electrons and holes. Among the several methods examined to date, synthesis of heterostructured semiconductors [10–12], deposition of zero-valent noble metal [13,14], non-metal ions doping [15,16] and metal ions doping [17,18] are the most reported widely. The coupling with narrow band gap semiconductors, such as metal sulfides and metal oxides, can promote charge separation and reduce the band gap of TiO_2 to improve the absorbance of visible light [19]. Modified by depositing zero-valent noble metal on the surface of TiO_2 forms Schottky barrier at the metal-TiO_2 interface, and that reduces the recombination of photogenerated electron-hole pairs and improves the photocatalytic performance [20]. Non-metal ions dopants can replace oxygen atom of TiO_2 crystal lattice during the non-metal ions doping process, thereby broadening the valence band and decreasing band gap energy [21]. Doping with metal ions can form defects in TiO_2 crystal lattice and change crystallinity to reduce the recombination of photogenerated electron-hole pairs and

---

[*] Corresponding author.
E-mail addresses: maxy@emails.bjut.edu.cn (X. Ma), zrsun@bjut.edu.cn (Z. Sun), huxiang99@163.com (X. Hu).

https://doi.org/10.1016/j.mssp.2018.05.026
Received 19 December 2017; Received in revised form 17 May 2018; Accepted 20 May 2018

prolong the lifetime of photogenerated carriers [22].

Co-doping is an effective method to improve the absorption in the visible spectral range via doping with multiple ions on the modification of TiO_2, because co-doping can passivate the defect bands produced by mono-doping [23]. Recently, co-doping TiO_2 with non-metal anions (such as B-N and C-N) [24,25], non-metal anions and metal cations (such as N-Mo, W-N and Cr-C) [23,26,27] and metal cations (such as Al-Fe, Sm-Ce and Mg-La) [28–30] have been studied to enhance the visible light photocatalytic and photoelectrocatalytic capacity.

Among these technologies, co-doping with multiple metal cations is one kind of effective and convenient method applied to modification of TiO_2. Tin (Sn) and molybdenum (Mo) have been found to be promising dopants to improve photocatalytic performance of TiO_2 by changing crystal structure. Ti^{4+} in the TiO_2 lattice can be replaced by Sn^{4+} and Mo^{6+} attribute to the ionic radii of Sn^{4+} (0.69 Å) and Mo^{6+} (0.62 Å) are similar to Ti^{4+} (0.68 Å) [31,32], which leading to less structural modification. The proper selection of dopants can induce enhanced the absorption of visible light with minimum structural modification [33]. The studies of Sn or Mo mono-doped TiO_2 [34,35] and Mo-N, Mo-C, Sn-Ag, and Sn-Ce co-doped TiO_2 [23,36–38] have been reported in the literature. However, few studies of Sn-Mo co-doped TiO_2 and the application in photoelectrocatalysis are reported.

In this work, a modified TiO_2 nanotube array electrode doped with Sn and Mo via single-step anodization process of Ti plate at a constant voltage was prepared. The preparation conditions of the electrode were investigated by chronoamperometry. The morphology and structure were characterized by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The optical property was investigated by UV–vis diffuse reflectance spectra. Subsequently, the photoelectrocatalytic activity of modified TiO_2 nanotube array electrode was evaluated under simulated sunlight irradiation against phenol, and the degradation process was studied.

2. Experimental details

2.1. Chemicals

A Ti plate (0.5 mm thick, 99.6% purity) was supplied by Kobe Steel., Ltd., Japan. Sodium stannate ($Na_2SnO_3{\cdot}3H_2O$) and sodium molybdate ($Na_2MoO_4{\cdot}H_2O$) was purchased from Tianjin Guangfu Fine Chemical Research Institute, China. NH_4F, hydrofluoric acid (HF, 40 wt%), nitric acid (HNO_3, 68 wt%), ethylene glycol (EG), isopropanol, ethanol absolute, acetone, and phenol were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were analytical grade and all solutions were prepared with deionized (DI) water (Milli-Q purification system, 18.2 MΩ cm).

2.2. Pretreatment of Ti substrate

The Ti plate was first mechanically polished with different type abrasive papers (with the following grades: 360, 500, 1000, and 2000), rinsed with DI water, and then immersed in acetone, isopropanol, and ethanol absolute orderly with ultrasonication for 15 min in each solvent. The pretreated Ti plate was stored in absolute ethyl alcohol.

2.3. Preparation of modified TiO_2 nanotube arrays

The pretreated Ti plate was etched in a mixture solution containing HF, NH_4F, and HNO_3 (0.85 g NH_4F was added into $HF/HNO_3/H_2O$ mixture solution) for 30 s and rinsed with DI water. The ratio of $HF/HNO_3/H_2O$ in the mixture solution was 0.5:4:5 in volume. TiO_2 nanotube arrays modified with Sn and Mo were prepared by a single-step anodization method using an etched Ti plate as anode and a Pt foil as cathode under a constant voltage. The electrolyte was prepared by mixing EG (96 vol%), H_2O (4 vol%), 0.5 wt% NH_4F, $Na_2SnO_3{\cdot}3H_2O$, and $Na_2MoO_4{\cdot}H_2O$. During the anodization process, the electrolyte was stirred continuously with a magnetic bar. After anodization, the as-prepared sample was annealed in muffle furnace under air atmosphere for 2 h at a heating rate of 2 °C min^{-1} to obtain Sn and Mo co-doped TiO_2 nanotube arrays. For comparison, a TiO_2 nanotube arrays without doping was also fabricated by anodization of Ti plate.

2.4. Photoelectrocatalytic experiments

Photoelectrocatalytic degradation of phenol was performed with a three electrode system under a constant bias voltage. The Sn-Mo-TiO_2 NTs/Ti electrode, Pt foil, and Hg/Hg_2SO_4 were used as working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. The Sn-Mo-TiO_2 NTs/Ti electrode was illuminated by a 300 W xenon lamp (HSX-F300, Beijing NBET Technology Co., Ltd, China) with a simulated AM 1.5 filter. The effective luminous intensity of the xenon lamp was 100 mW cm^{-2}. The simulated sunlight illuminated on Sn-Mo-TiO_2 NTs/Ti electrode through a transparent quartz window. The electrolyte was 0.05 mol L^{-1} Na_2SO_4 solution containing 50 mg L^{-1} phenol. During the degradation process, the electrolyte was stirred continuously with a magnetic bar at 400 rpm. The concentration of phenol and degradation intermediate products were determined by a high performance liquid chromatography (HPLC, Waters 1525, USA) with a Waters 2489 dual λ UV/Visible detector. The concentration of phenol and aromatic intermediate products were determined with a Waters X-Terra® MS-C18 chromatographic column (4.6 × 250 mm, 5 µm particle size). The mobile phase was 37.5% methanol and 62.5% water with flow rate of 0.8 mL min^{-1}. The detection wavelengths used for phenol and aromatic intermediate products analyses were 275 and 295 nm, respectively. The short chain organic acids were determined with a Waters X-Select® HSS T3 chromatographic column (4.6 × 250 mm, 5 µm particle size). The mobile phase was 0.1 vol% phosphoric acid with flow-rate of 1 mL min^{-1}. The detection wavelength used for short chain organic acids was 213 nm. Total organic carbon (TOC) was analyzed by TOC analyzer (Vario TOC cube, Elementar, Germany).

The conversion efficiency (η) of phenol was calculated using the following equation:

$$\eta = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where C_0 is the initial phenol concentration and C_t is phenol concentration at photoelectrocatalytic degradation time *t*.

The % TOC removal (φ) was calculated using the following equation:

$$\varphi = (TOC_0\text{-}TOC_1)/TOC_0 \times 100\% \quad (2)$$

where TOC_0 is the initial TOC value and TOC_1 is TOC value at the end of the photoelectrocatalytic reaction.

2.5. Analysis and characterization

The surface and cross-section morphologies of the electrode and chemical composition were studied using field emission scanning electron microscopy (FESEM, Hitachi SU-8020, Japan) combined with energy dispersive spectroscopy (EDS, X-Max^N 80, Oxford Instruments). The crystallite structure of the modified TiO_2 NTs was analyzed by X-ray diffraction (XRD, Bruker AXS D8 Advance, Germany). The binding energy was identified by X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific, ESCALAB 250, USA) with Al-Kα radiation. UV–vis diffuser reflectance absorbance spectra were obtained by UV–vis spectrophotometer (Hitachi U-3900H, Japan). Electrochemical and photoelectrochemical performence of Sn-Mo-TiO_2 NTs/Ti electrode were investigated by the electrochemical workstation (Metrohm AutoLAB PGSTAT302N, Switzerland) in Na_2SO_4 solution with a three electrode system consisting of a Sn-Mo-TiO_2 NTs/Ti electrode as the working electrode, a Pt foil as the counter electrode and a Hg/Hg_2SO_4 as the reference electrode.