Materials Science and Engineering B 187 (2014) 39–45

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Preparation of an Fe-doped visible-light-response TiO_2 film electrode and its photoelectrocatalytic activity

Wenwei Tang[a],*, Xiaoying Chen[a], Jin Xia[a], Jiemin Gong[a], Xinping Zeng[b],*

[a] Department of Chemistry, Tongji University, Shanghai 200092, China
[b] School of Life Sciences and Technology, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:
Received 7 December 2013
Received in revised form 17 March 2014
Accepted 28 April 2014
Available online 13 May 2014

Keywords:
Fe-doped TiO_2 film electrode
Visible-light response
Photoelectrocatalysis
Methyl orange
Rhodamine B

ABSTRACT

Fe-doped TiO_2 film electrodes were prepared by sol–gel and dip-coating methods, and their photoelectrocatalytic properties were investigated under both ultraviolet and visible light through degradation of methyl orange and Rhodamine B. The results showed that the Fe-doped TiO_2 film electrodes mainly consisted of anatase TiO_2. The Fe-doping effectively restrained the grain growth of TiO_2 and the phase transformation of rutile. The modified film substantially extended the photo response from 452 nm to 604 nm and band gap decreased to 2.05 eV. The photocatalytic performance of the Fe-doped TiO_2 film electrode was enhanced. The response current of 1% Fe-doped TiO_2 film electrode was 30.3 μA while TiO_2 film electrode had no response under visible light. The decolorization rate of RhB by 1% Fe-doped TiO_2 film electrode was 22% higher than that of undoped electrode, which indicated that the extended responsive wavelength range greatly expanded the application potential of the modified electrode.

1. Introduction

Visible-light responsive photocatalytic technology has attracted widely attention because it can make full use of solar energy and eliminate undesired chemical substances for environmental conservation [1,2]. Titanium dioxide (TiO_2), as a semiconductor with a wide band gap, is one of the most promising photocatalytic materials in the area of environmental protection because of its superior properties in photo-conversion and photocatalysis [3,4]. In addition, the advantages of TiO_2 include operation simplicity, moderate reaction conditions, high degradation efficiency, easy automation and no secondary pollution [5].

However, the dominant light absorption of TiO_2 is in the UV range due to its wide band gap, which greatly limits its industrial application as there is only 4% UV light in sunlight. Meanwhile, its high recombination rate of electron–hole (e–h) pairs also leads to a low number of active free radicals and photocatalytic efficiency [6].

Efforts have been made over the past decades to develop nano-TiO_2 photocatalysts. Yang et al. [7] prepared a TiO_2/carbon membrane via a sol–gel process, coating TiO_2 in a reactor used as an electrocatalyst. Wu et al. [8] immobilized TiO_2 onto a titanium electrode to conduct methyl tert-butyl ether degradation in aqueous solution. To substitute the UV light with visible light or sunlight, doping metals or non-metal elements are promising approaches to increase the photocatalytic activity. Peng et al. [9] discovered that S-doped TiO_2 films exhibited excellent photocatalytic activity comparing to pure TiO_2 films because of their surface microstructure. Liu et al. [10] prepared N–doped TiO_2 nanotube arrays through electrochemical anode oxidation using N_2–plasma etc. as material, which resulted in a significant enhancement of the photocatalytic activity under visible light. Zhang et al. [11] found that non-calcined Fe-doped TiO_2 film caused higher photocatalytic degradation of MO, which could be described as a pseudo-first order reaction. Ostovari et al. [12] applied an atmospheric pressure chemical vapor deposition (APCVD) method to prepare Fe-doped TiO_2 consisted of anatase and rutile phases. It showed a considerable enhancement in the wettability of the ferromagnetic nanostructure when applying a magnetic field under UV and visible light. Su et al. [13] investigated the nitrogen and Fe co-doping TiO_2, which showed a narrow band gap and significantly improved photocatalytic activity under visible irradiation. Meanwhile, the density functional theory (DFT) calculations indicated that the co-doping of nitrogen and Fe induced the formation of new states between the valence band and the conduction band.

Efforts also have been made to develop nano-TiO_2 photoelectrocatalytic (PEC) oxidation. Compared to the traditional photocatalysis, an external bias potential is helpful for restricting the recombination of electron/hole pairs via an external circuit,

---

* Corresponding authors. Tel.: +86 02165983366; fax: +86 02165983366.
E-mail addresses: tangww@tongji.edu.cn (W. Tang), zengxp@tongji.edu.cn (X. Zeng).

http://dx.doi.org/10.1016/j.mseb.2014.04.011
0921-5107/

consequently improving the photocatalytic efficiency [14]. Doping is a popular method, by this way, the band gap of TiO_2 narrowed and the photocatalytic activity was improved [15,16].

In the present study, the sol–gel method was used to prepare the Fe-doped TiO_2 film electrodes. Their photoelectrocatalytic properties were investigated under UV and visible light irradiation using MO and RhB as model pollutants, and the results showed improved photocatalytic properties and the application potential of the modified electrode.

2. Materials and methods

2.1. Preparation of Fe-doped TiO_2 film electrodes

Methyl orange (MO) and Rhodamine B (RhB) were purchased from Shanghai Dyeing Plant (Shanghai, China), and all chemicals were of analytical purity. Ti sheet was chosen as the Ti substrate (20 mm × 30 mm × 1 mm) from Shanxi Ti Company (Shanxi, China). The Ti substrate was polished, ultrasonically cleaned in detergent and acetone, and detarnished under acid etching followed by washing with distilled water, and finally sealed under anhydrous ethanol [17].

Fe-doped TiO_2 was synthesized using a sol–gel method. In a typical synthesis, three components (A–C) were respectively prepared at first. For component A, 5 mL isopropanol was added into 10 mL tetrabutyl titanate with 3 mL acetylacetone at ambient temperature, and stirred for 30 min. Component B consisted of 2 mL distilled water and 2.5 mL isopropanol, a thimbleful of ethanolamine, which served as a regulator, and different amounts of ferric nitrate according to $n\mathrm{Fe}/n\mathrm{Ti} = 0$, 0.1%, 0.2%, 0.5%, 1.0% and 2.0% (0, 0.0119, 0.0237, 0.0594, 0.1187 and 0.2374 g, respectively). Component C was obtained by dissolving an appropriate amount of polyethylene glycol in 2.5 mL isopropanol to avoid agglomeration of particles and increase the hydrophilicity. Then component B was added dropwise into component C under vigorous stirring and followed by dropwise addition of component A. The mixture was stirred for another 30 min and aging overnight to obtain the soliquid.

The Fe-doped TiO_2 film electrode was prepared by the dip-coating method due to its low cost and controllability. Ti sheet was cleaned and vertically dipped into the soliquid for 5 min, then elevated at a certain speed and dried under an infrared lamp for 10 min to form a gel. The film electrode was annealed at 500 °C for 30 min in a muffle furnace after 5 times of dip-coatings to guarantee the coating layer oxidized completely. Finally, when 15 layers were coated onto the electrode, the last annealing time was prolonged to 2 h to acquire a modified anatase TiO_2 film electrode.

2.2. Test methods of the Fe-doped TiO_2 film electrode

X-ray diffraction (XRD) patterns were obtained from a Bruker Foucs D8 X-ray diffractometer with Cu Kα radiation in a 2θ range of 10–70°.

The Raman spectra were collected using Renishaw Invia confocal microscopic Raman spectroscopy. Its optical efficiency was more than 30%, the spectral resolution was 1 cm^{-1}, the laser wavelength was 514 nm, and Raman shift range for tests was 100–1000 cm^{-1}.

The UV–vis diffuse reflectance spectra were measured in the wavelength range from 300 to 800 nm using an Agilent 8453 UV–vis spectrometer.

The morphologies of the Fe-doped TiO_2 film electrodes were observed by a Hitachi S-4800 scanning electron microscope.

An Autolab model PGSTAT30 electrochemical workstation was used to test the electrochemical performances of the electrodes. The prepared electrode was used as the working electrode (20 mm × 30 mm), the platinum electrode was used as the counter electrode (4 mm × 15 mm × 15 mm), and a saturated calomel electrode (SCE) was used as the reference electrode. All the photocatalytic and electrocatalytic tests were performed in 60 mL 0.5 mol/L Na_2SO_4 solution. The equilibrium time for chronocoulometry (C–C) test was 2 s, time interval was 0.1 s, the potential duration was 0.25 V s^{-1}, the bias voltage applied to the working electrode was 1 V under the UV pulse and 2 V under the visible light pulse. For the electrochemical impedance spectroscopy (EIS) test, the frequency range was 10,000–0.1 Hz and the electric potential of the amplitude was 50 mV.

2.3. Photocatalytic activity test

For the UV photocatalytic activity test, a 56 W Phillips UV lamp was used as the UV light source with a main emission at 365 nm, and the objective degradation pollutant was 60 mL 30 mg/L MO solution; For the electrocatalytic activity test, 1 V external bias potential was applied between the working electrode and the counter electrode; For the UV photoelectric activity test, a 56 W Phillips UV lamp was used as the UV light source and 1 V external bias potential was applied.

For the visible photoelectric activity test, a 300 W Xenon arc lamp was used as the visible light source with UV cut off (wavelength < 400 nm), 2 V external bias potential was applied between the working electrode and the electrode and the objective degradation pollutant was 60 mL 10 mg/L RhB solution.

The whole degradation process was conducted in a beaker containing different objective degradation pollutants and connected to a condensate pipe with continuing cooling water. The degradation was operated under UV and visible light for 3 h, respectively. A UV–vis spectrometer was used for whole wavelength scanning. The maximum absorptive wavelength of MO was 465 nm and that of RhB was 553 nm. The concentration after degradation was determined by an Agilent 8453 UV–vis spectrometer. The calculation of the decolorization rate for MO and RhB was:

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100\% \qquad (1)$$

η is the decolorization rate of dye (%); C_0 is the initial concentration (mg/L); C is the final concentration (mg/L).

3. Results and discussions

3.1. Characterization of the Fe-doped TiO_2 film electrode

3.1.1. XRD

The XRD patterns of the TiO_2 film electrode samples were shown in Fig. 1, of which the molar ratios between Fe and Ti were 0, 0.1:100, 0.2:100, 0.5:100, 1.0:100 and 2.0:100.

The pure TiO_2 film electrode exhibited the characteristic peaks of anatase (major peaks: 25.6°, 37.8° and 48.3°) and rutile (major peaks: 27.4° and 35.5°). However, other crystalline phases, such as Fe_2O_3, were not observed, which revealed that the iron ions might substitute titanium in the TiO_2 matrix at high temperature calcinations or locate interstitially to form a Fe-TiO_2 solid solution due to the similar ionic radius of Fe^{3+} and Ti^{4+} [18,19]. Fe-doping did not change the anatase phase of TiO_2 but inhibited the formation of rutile TiO_2 with an increase of the Fe contents, which was in accordance with a previous study [20].

According to the Scherrer equation, $D = k_s\lambda/\beta\cos\theta$, where D is the crystal size, k_s is the Scherrer constant, λ is the X-ray wavelength, β is the full width at half maximum and θ is the diffraction angle. The calculation in Table 1 indicated that Fe doping had the