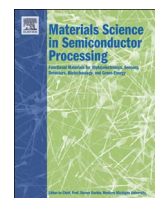




ELSEVIER

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

5,10,15,20-tetrakis(4-chlorophenyl)porphyrin decorated TiO₂ nanotube arrays: Composite photoelectrodes for visible photocurrent generation and simultaneous degradation of organic pollutant



Cui Han, Qian Shao*, Mei Liu, Shengsong Ge, Qingyun Liu, Jing Lei

College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, PR China

ARTICLE INFO

Article history:

Received 5 February 2016

Received in revised form

26 June 2016

Accepted 18 August 2016

Keywords:

H₂TCIPP-TNTs photoelectrode

Photoelectrochemical performance

Photocatalytic activity

ABSTRACT

The composite TiO₂ nanotube arrays/5,10,15,20-tetrakis(4-chlorophenyl) porphyrin (H₂TCIPP-TNTs) photoelectrode with high visible light photoelectrochemical properties was prepared by a facile surface adsorption method. The morphology, composition and optical property of H₂TCIPP-TNTs photoelectrode was investigated by scanning electron microscopy, X-ray diffraction, FT-IR spectra, X-ray photoelectron spectroscopy and UV–vis diffuse reflectance spectroscopy. The sensitization of H₂TCIPP on TNTs significantly extended the visible light response, the as-prepared H₂TCIPP-TNTs photoelectrode exhibits excellent photoelectrochemical performance and photocatalytic activity. The photodegradation efficiency of rhodamine B by using H₂TCIPP-TNTs irradiated under visible light for 4 h was up to 92.8%, which was higher than that of pure TiO₂ nanotube arrays.

© Published by Elsevier Ltd.

1. Introduction

In recent years, TiO₂ nanoparticles showed enormous potential as environment-friendly and economical photocatalysts for the treatment and purification of a large variety of pollutants, especially for the decomposition of toxic organic compounds [1–3]. Compared with traditional TiO₂ nanoparticles, TiO₂ nanotube arrays have been typically and widely used in photoelectrode, biomedicine, environmental purification, sensor and solar cell [4–10] owing to its high regulation, larger surface area and pore volume, unidirectional charge transfer and transportation, excellent controllability [11–14]. It is well known that TiO₂ nanotube arrays can now be fabricated by a number of advanced techniques such as anodization [15], template technique [16], hydrothermal process [17] and soft chemical process [18]. Among these fabrication techniques, the electrochemical anodization process, since its discovery, has been considered as the most prominent one in producing high aspect-ratio nanotubes with controllable tube size and morphology [19,20].

However, practical applications of TiO₂ are severely hampered by its large band gap, which can only be activated under UV irradiation [21], and the high recombination rate of photogenerated electron-hole pairs is another main drawback limiting the further improvement of photoelectric properties [22]. Therefore, many

methods have been applied to extend the visible light absorption and to reduce the recombination of TiO₂, such as metal ions [23,24] and non-metallic species [25,26] doping, surface modifications with noble metal [27,28] and semiconductor [29,30]. Nevertheless, the above modifications still have some inherent problems unresolved. For instance, the doping N into TiO₂ crystal structures by heating treatment under NH₃ flow requires expensive and complex equipment, and the high stability and uncontrollable doping content is adverse factors of TNTs for photoelectronic applications [31]. The sensitizations with inorganic quantum dots, specifically CdS semiconductors, also pose environmental hazards due to the dissolution or photocorrosion during the photocatalytic progress [32]. Compared with inorganic sensitizers, porphyrins and their derivatives have been considered as environmental friendly photosensitizers because they contain no metal elements and show an intense harvesting in the visible light region, which attract immense attention in visible light photocatalytic degradation of toxic organic pollutants [33,34]. Specifically, porphyrins on anatase-TiO₂ are used as photosensitizers, which also benefit the formation of sensitizer-semiconductor interfaces for highly effective electron transfer and charge separation [35–38]. Recently, Wei et al. [39] prepared meso-tetra(4-carboxyphenyl) porphyrin (H₂TCPP) sensitized TiO₂ nanotube arrays by immersing the TNTs into H₂TCPP solution, and the as-prepared H₂TCPP-TiO₂ nanotube samples showed the high visible light absorption and low electron-hole pair recombination. In addition, asymmetric zinc-porphyrin (ZnPy) was applied to sensitize nanosized TiO₂, the 1.0% ZnPy-TiO₂ exhibited strong

* Corresponding author.

E-mail address: shaoqian01@126.com (Q. Shao).

absorption in the visible-light region [40]. Therefore, porphyrins as photosensitizers are a meaningful attempt for the visible light utilizations of TNTs. Despite the progresses made thus far in previous studies, noteworthy, up to now, there have still been very limited systematic studies on the photocatalytic activity and photoelectrochemical performance of the porphyrins sensitized TiO₂ nanotube arrays.

In this paper, we successfully prepared H₂TCIPP-TNTs photoelectrode by a facile surface adsorption method. The TiO₂ nanotube arrays with an inner diameter of approximately 100 nm were prepared by a two-step anodization at 20 V for 3 h, and the photoelectrochemical performance of the H₂TCIPP-TNTs photoelectrodes was systematically explored in terms of the H₂TCIPP content in order to assess the optimal photocatalytic decomposition of rhodamine B (RhB) molecules. In addition, the charge carrier transportation mechanism of H₂TCIPP-TNTs photocatalysts was proposed to show the high visible light photocatalytic property.

2. Experimental

2.1. Preparation of TiO₂ nanotube arrays

TiO₂ nanotube arrays were made via a two-step anodization method including Ti foil (99% pure, thickness 0.2 mm, Tianjin Gerui Co., Ltd, China) acting as the anode, similar to the previous report [41]. The electrolyte consisted of 0.5 wt% NH₄F dissolved in a mixture electrolyte of ethylene glycol and de-ionized water (0.3 wt% H₂O). The synthesis process was conducted at the room temperature. The first-step anodization was performed under a constant voltage of 60 V for 2 h, and the as-formed oxide layer was peeled subsequently by ultrasonic bath after rinsing by distilled water and absolute ethanol. The second-step anodization was conducted at 20 V for 3 h. After being dried in air, samples were annealed at 450 °C for 3 h at a heating rate of 2.5 °C/min.

2.2. Preparation of H₂TCIPP-TNTs photoelectrode

5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin (H₂TCIPP), Fig. 1, was prepared according to published procedures [42,43]. The identification of synthesized H₂TCIPP was well supported by ¹H NMR analysis (See Supporting Information). The adsorbed amounts of H₂TCIPP on TNTs were adjusted by changing the concentration of H₂TCIPP solutions and the immersion time of TNTs in H₂TCIPP solutions. In a typical synthesis, the as-prepared

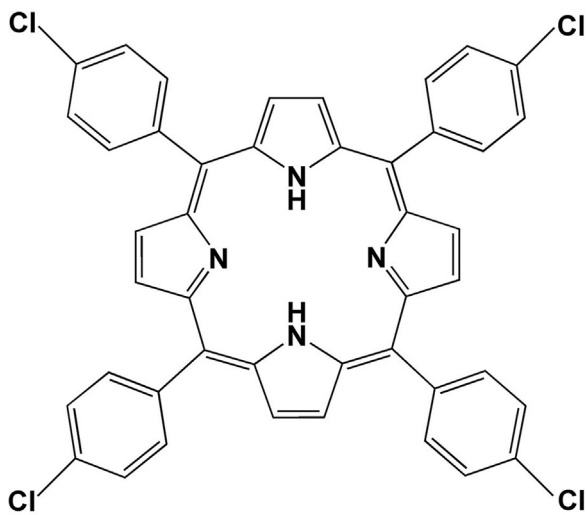


Fig. 1. The molecular structure of porphyrin (H₂TCIPP).

TiO₂ nanotube arrays (1 × 1 cm² in photoactive area) were immersed into 2.5 mmol/L H₂TCIPP solution in trichloromethane for 24 h. Meanwhile, a series of H₂TCIPP-TNTs photoelectrodes with different H₂TCIPP amounts were fabricated to evaluate the influence of H₂TCIPP on photoelectrochemical performances of TNTs, and these samples were marked as H₂TCIPP-TNTs (a, b) to designate the samples prepared in a mmol/L H₂TCIPP solution for b h.

The amount of adsorbed H₂TCIPP on TiO₂ nanotube arrays was determined by UV/vis absorption spectral measurement of the concentration changes of the H₂TCIPP solution before and after adsorption. First, the calibration curve was made by A versus c according to the Lambert–Beer law, the absorbance of H₂TCIPP in trichloromethane was determined at λ_{max} = 419 nm. Then the as-prepared TiO₂ nanotube arrays (2.54 cm²) were immersed into 25 mL H₂TCIPP solution (2.5 mmol/L) for 24 h. In order to make the absorbance of H₂TCIPP solution before and after adsorption conformed to the linear of calibration curve, the concentration of H₂TCIPP solution was diluted 2000 times.

2.3. Characterization

All the measurements in this work were conducted at room temperature. The morphology of the samples was examined by a scanning electron microscopy (SEM, SU-70, Japan) at an acceleration voltage of 30 kV. The cross-sectional thickness measurements were carried out on mechanically bent cracked samples. The crystallographic information of the samples were analyzed by a X-ray diffraction (XRD, Rigaku D/Max2500PC, Japan) using Cu Kα radiation (λ = 0.15418 nm), with the scanning rate of 4°/min in 2θ range from 10°–70°. Fourier transform infrared (FT-IR) spectra were measured by using a NICOLTE380 FT-IR spectrometer (Thermo, USA) with KBr as the reference. X-ray photoelectron spectroscopy (XPS) measurements were performed with an X-ray spectrometer PHI 5300 (Perki-El2 met, USA), using Mg Kα X-ray radiation (1486.6 eV). UV–vis diffuse reflectance spectra of the samples were recorded on a UV–vis spectrophotometer (UV–vis DRS, UH4150, Hitachi, Japan) with an integrating sphere attachment, Al₂O₃ was used as a reflectance standard in the wavelength range of 200–800 nm.

2.4. Photoelectrochemical performance evaluation

Photoelectrochemical performances of the as-prepared samples were measured with an electrochemical workstation (LK2005A, LANLIKE Co., Ltd., Tianjing, China) using a three-electrode system composed of the H₂TCIPP-TNTs with 1 cm² surface area as a working electrode, a platinum electrode as a counter electrode, a saturated calomel electrode as a reference electrode. A mixture electrolyte solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃ was employed to investigate the photoelectrochemical performances of these photoelectrodes. The working electrode was illuminated with a solar simulator equipped with a 300 W Xe lamp with a visible-light filter (> 420 nm). The transient photocurrent of the working electrodes was recorded according to the responses to sudden switching on and off at 0.25 V bias.

2.5. Photocatalytic Activity Test

The photocatalytic activity of the sample was evaluated by the photocatalytic degradation of a model pollutant RhB. The Xe lamp (300 W) was used as a visible light source and kept the temperature of above aqueous solution at 25 °C. The distance between the light source and the reactor is 10 cm. The as-prepared photoelectrodes (10 cm²) were used and hanged in 30 mL of RhB aqueous solution (conc.: 5 mg/L). At certain time intervals, the degradation efficiency was determined using a spectrophotometer,

Download English Version:

<https://daneshyari.com/en/article/7118350>

Download Persian Version:

<https://daneshyari.com/article/7118350>

[Daneshyari.com](https://daneshyari.com)