



A silicon-doped TiO₂ nanotube arrays electrode with enhanced photoelectrocatalytic activity

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ABSTRACT

Silicon-doped titania nanotube arrays were fabricated by electrochemical anodization on a Ti sheet, followed by chemical vapor deposition (CVD) treatment using tetraethylorthosilicate as silicon source. The highly ordered nanotube arrays obtained by anodization kept its nanotube-like structural integrity after CVD treatment. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) results revealed that the introduced silicon might be incorporated into titania matrix. This incorporation helped to increase the thermal stability of titania, which was in favor of suppressing the phase transformation from anatase into rutile and also inhibiting the growth of anatase crystallite of titania at high calcination temperature. A significant blue-shift was observed in the spectrum of UV absorption. The surface of Si-doped TiO₂ nanotube arrays showed a super-hydrophilic behavior under UV illumination. For Si-doped TiO₂ nanotube electrode, the maximum photoconversion efficiencies of 31.8% under high-pressure mercury lamp irradiation and 16.5% using an optical filter (280–400 nm) under the same lamp irradiation were achieved, which were obviously higher than those of undoped one. The photoelectrocatalytic (PEC) activities were investigated using pentachlorophenol (PCP) as a probe substance. Compared with undoped TiO₂ nanotube electrode, the Si-doped TiO₂ showed better PEC capability in the degradation of PCP under high-pressure mercury lamp irradiation.

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1. Introduction

Titanium dioxide (TiO₂) has been regarded as the most promising photocatalyst for its low cost, non-toxicity, high stability and high efficiency in degrading difficult-to-remove organic pollutants. However, the photocatalytic oxidation technology involving TiO₂ photocatalysts always suffers from the difficulties of separating suspended TiO₂ nanoparticles from aqueous solution as well as low quantum yield caused by the rapid combination of photogenerated electrons and holes [1]. In comparison, the immobilized TiO₂ film on a solid carrier by spin [2] or dip-coating [3] methods is more desirable in its photocatalytic application, whereas it still has defects such as poor adhesion of TiO₂ film to supporting carriers [4] and low surface area of supported TiO₂ photocatalyst exposed to solution. Accordingly, TiO₂ nanotube-array film growing on Ti substrate by anodization process appears a progress compared to immobilized TiO₂ film. As an integrative electrode, nanotubular TiO₂ film possesses good mechanical adhesion strength and electronic conductivity, and

also provides greater surface area for photoelectrochemical action. Particularly, the tubular structure makes the regions both inside and outside the tubes (intertubular region) easily accessible to the redox couples in the electrolyte and also offers the ability to influence the absorption and propagation of light by precisely designing and controlling the geometrical parameters of the architecture [5,6]. The method to prepare such highly ordered nanotube arrays, based on anodization of Ti in fluorinated electrolytes, has been reported in recent years [7–9]. Furthermore, the thickness and morphology of such a nanotubular TiO₂ film could be easily controlled by tailoring the anodization conditions such as applied potential, anodization duration and electrolyte composition [10–13]. In our previous work, a well-aligned TiO₂ nanotube arrays has been prepared in diluted HF-containing electrolytes, which exhibited better photoelectrocatalytic activity and higher photoconversion efficiency than immobilized TiO₂ film [14]. Considering such properties, TiO₂ nanotube arrays are worthy of careful scientific consideration in photocatalytic oxidation application.

The doping of TiO₂ with different metal elements such as Pt, Ag and Fe [15–17] or with selected non-metal elements such as N, C and B [18–20], was proved to either improve photocatalytic activity of TiO₂ under UV irradiation or extend the photoresponse

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of TiO₂ further into visible light region. Embedding a special element Si into TiO₂ matrix has been found to induce new structural and physicochemical properties such as high thermal stability, quantum-sized crystalline and good surface wettability [21,22]. Iwamoto et al. [23] prepared silicon-modified titania photocatalyst with glycothermal method, and confirmed that the incorporation of silicon atoms into TiO₂ matrix increased thermal stability and decreased the crystallite size of the silicon-modified titania. Park and co-workers [24] reported the effect of Si-doping on photocatalytic behavior of TiO₂, and suggested the enhanced photoactivity was attributed to the increase of surface area and crystallinity through embedding amorphous silica into titania. Undeniably, modification of TiO₂ with silicon atoms opens up new possibilities for the development of photocatalytic material. The current investigations for photoactivity and photochemical properties of Si-doped TiO₂ are mainly carried out using its powdery form. It is expected that combining small-sized anatase crystallite of Si-doping TiO₂ with unique nanotubular structure would exhibit an improved photoactivity. To the best of our knowledge, however, there are no reports so far regarding Si-doped TiO₂ nanotube arrays electrode and its photoelectrocatalytic characteristics.

In this research, we fabricated a novel Si-doped TiO₂ nanotube arrays which possessed a highly ordered and vertically oriented morphology. Incorporation of silicon atoms into TiO₂ matrix was carried out by chemical vapor deposition treatment after anodization process. The objectives of this research were to investigate the structural characteristics and surface morphology of the Si-doped TiO₂ nanotube arrays and to measure its photoelectrochemical capability. Pentachlorophenol (PCP), used extensively as wood preservatives and pesticides, was chosen as the probe substance to evaluate the photocatalytic (PC) and photoelectrocatalytic (PEC) activities of Si-doped TiO₂ nanotube array electrode. It is expected that this new type of electrode, constituted of highly ordered nanotube arrays owning large surface area as well as silicon dopant modification, might rather enhance PC and PEC activities.

2. Experimental details

2.1. Preparation of Si-doped TiO₂ nanotube arrays

The titanium sheets (0.5 mm thick, 99.6% purity, from Tianjin Gerui, China) were mechanically polished with different abrasive papers, rinsed in an ultrasonic bath of ethanol for 5 min and deionized water for 15 min in turn, and then chemically etched by immersing in a mixture of HF and HNO₃ (HF:HNO₃:H₂O = 1:4:5 in volume) for 20 s, and finally rinsed in deionized water. The substrate was dried in a N₂ stream at room temperature.

The anodization was performed in a two-electrode electrochemical cell with a direct current power supply (Beijing Dahua Wireless Instrument Company, China, 0–100 V) at room temperature. The anodizing voltage varied from 0 to 20 V with increasing rate of 100 mV s⁻¹ and was kept at 20 V for 2 h, with a Ti sheet serving as the anode and a Pt foil serving as the cathode. The electrolyte was 0.5 wt.% NH₄F + 1 M (NH₄)₂SO₄ aqueous solution [7]. The pH of the electrolyte was adjusted at 6 ± 0.5 by a mixture solution of 2 M H₂SO₄ + 0.5 wt.% NH₄F during the entire process. After anodization, the sample was immediately rinsed with deionized water and dried with a N₂ stream. Then it was annealed at 450 °C in air for 3 h with heating and cooling rates of 2 °C min⁻¹ to convert the amorphous phase to the crystalline one. Silicon atoms were introduced into the TiO₂ nanotube arrays with chemical vapor deposition (CVD) technique in a quartz tube. As silicon source, tetraethylorthosilicate (TEOS) was admitted to the tube furnace carried by Ar gas with

controlled gas flow at 500 °C for 15 min, and the concentration of silicon is about 156 mg L⁻¹. After deposition, the sample was annealed at 650 °C for 30 min. In addition, undoped TiO₂ nanotubes were prepared under the identical thermal conditions in air flow for comparison.

2.2. Characterization

The morphology was investigated using an environmental scanning electron microscope (ESEM; Quanta 200 FEG) with an accelerating voltage of 30.0 kV. The crystalline structure of the prepared nanotube samples were determined by X-ray diffraction (XRD) using a diffractometer with Cu K α radiation (Model, Shimadzu LabX XRD-6000). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The chemical composition of the Si-doped sample was analyzed by X-ray photoelectron spectroscopy (XPS; Escalab 250) with a monochromatic Al K α source. Light absorption properties were characterized using UV–vis diffuse reflectance spectra (JASCO, UV-550) with a wavelength range of 190–800 nm. The surface wettabilities of Si-doped and undoped samples were measured using a contact angle meter (Data physics OCA 20 Contact Angle System).

2.3. Photoelectrochemical measurements

Photocurrent densities were measured using a CHI electrochemical analyzer (CH instruments 650B, Shanghai Chenhua, China) in a standard three-electrode configuration with the Si-doped TiO₂ nanotube arrays as photoanode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. 1 M KOH purged with N₂ was used as the electrolyte. A 300 W high-pressure mercury lamp (Beijing Huiyixin, China) served as the UV-light source with a principal wavelength of 365 nm. In addition, an optical filter, which allowed transmission of the wavelength from 280 to 400 nm, was used for evaluating the photoelectrochemical activity of nanotube arrays under near UV irradiation. Incident light intensity (I_0) was measured by a radiometer (Photoelectric Instrument Factory Beijing Normal University, model UV-A) in mW cm⁻².

2.4. Photoelectrocatalytic experiments

The PEC degradation of PCP was performed in a single photoelectrochemical compartment. The Si-doped TiO₂ photoanode was in parallel with platinum foil cathode in a cuboid quartz reactor with magnetic stirring. The electrodes were connected to a CHI 650B electrochemical analyzer. The high-pressure mercury lamp was placed vertically outside the reactor. Bias potentials applied on photoanode were 0.2 V (vs. SCE) under UV illumination (with a maximum wavelength of 365 nm, $I_0 = 0.75$ mW cm⁻²). The initial concentration of PCP aqueous solution was 20 mg L⁻¹ with 0.01 M Na₂SO₄ as electrolyte (pH 7.0). The concentration of PCP was determined by HPLC (JASCO, UV-1575) with a Kromasil ODS (5 μ m, 4.6 mm \times 250 mm) reverse-phase column. The mobile phase was 1.0 ml min⁻¹ of methanol and water containing 0.5 vol% acetic acid (v:v = 0.85:0.15) and the wavelength was set at 254 nm.

3. Results and discussion

3.1. Morphology of Si-doped TiO₂ nanotube arrays

Fig. 1 shows ESEM images of undoped TiO₂ and Si-doped TiO₂ nanotube arrays, respectively. The obtained nanotube arrays show highly ordered and vertically oriented morphology with inner diameter from 50 to 65 nm. The inset of Fig. 1b gives the

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