



# Solvothermal preparation of Fe-doped TiO<sub>2</sub> nanotube arrays for enhancement in visible light induced photoelectrochemical performance



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## ARTICLE INFO

### Article history:

Received 12 May 2016

Received in revised form

25 July 2016

Accepted 26 July 2016

Available online 12 August 2016

### Keywords:

TiO<sub>2</sub> nanotube arrays

Fe<sup>3+</sup> doping

Visible light response

Photoelectrochemical performance

## ABSTRACT

Highly visible light active Fe-doped TiO<sub>2</sub> nanotube arrays (Fe-TiO<sub>2</sub> NTs) were prepared by a simple solvothermal method, and the morphology, composition, visible light response and photocatalytic property were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis diffraction reflection spectroscopy (DRS), photocurrent and photoelectrocatalysis (PEC) test. The results indicated that the doping progress of Fe<sup>3+</sup> ions didn't destroy the highly-ordered nanotube array structures, and Fe<sup>3+</sup> concentrations had significant influences on photoelectrochemical properties of TiO<sub>2</sub> NTs. The Fe-TiO<sub>2</sub> NTs prepared with the Fe<sup>3+</sup> concentration of 1 mmol/L exhibited more excellent photocurrent and PEC activities than those of TiO<sub>2</sub> NTs and other Fe-TiO<sub>2</sub> NTs under visible or solar light irradiation. The highly visible active Fe-TiO<sub>2</sub> NTs may show extensive applications in solar cells and photocatalysts due to the excellent photoelectrochemical performance.

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## 1. Introduction

In recent years, the overdevelopment of fossil fuels caused energy crisis and environmental pollution, which greatly damaged the progress of human society [1–3]. More and more scientists devote their investigations to explore various energy and environmental materials to solve these obstacles [4–6]. Titania (TiO<sub>2</sub>) has attracted considerable attention because its unique physical and chemical properties make it suitable for applications in the fields of solar cells and photocatalytic degradation of pollutants [7–9]. Comparable to TiO<sub>2</sub> nanoparticles, TiO<sub>2</sub> film photoelectrodes could significantly improve photoelectrochemical properties including the photoelectric conversion and photocatalysis. However, TiO<sub>2</sub> nanoparticles need to be deposited on indium tin oxide or fluorine doped tin oxide glass to form TiO<sub>2</sub> film photoelectrodes, and the disorder distribution of nanoparticles in TiO<sub>2</sub> films greatly limits the rapid transportation of photogenerated carries, which

greatly inhibits the improvement of the photoelectric transformation efficiency [10]. Moreover, the powder characteristic reduces the cyclic utilization of TiO<sub>2</sub> nanoparticles after photocatalytic progress. As excellent TiO<sub>2</sub> films, well aligned TiO<sub>2</sub> nanotube arrays (TiO<sub>2</sub> NTs) have drawn ever-increasing attention because they not only possess high surface areas but also offer the advantage of carrier transportation facilitating the collection of photogenerated electrons, and therefore are expected to be promising high-performance photoanodes for use in solar cells [11,12]. In addition, because TiO<sub>2</sub> NTs are grown from Ti substrates, the integrality makes the practical application simpler and more cost-effective as compared with TiO<sub>2</sub> powders, avoiding the filtration step after photoreaction or the immobilizing process required for photocatalyst particles [13].

However, owing to the large band gap (3.2 eV), it is well known that the photoelectrochemical activities of TiO<sub>2</sub> NTs are largely restricted to the ultraviolet (UV) region which only contributes to about 4% of the entire solar spectrum [14]. Several strategies have been adopted to extend the light response of TiO<sub>2</sub> NTs to the visible light region [15]. In order to resolve the above restriction and modify the electronic structure of TiO<sub>2</sub> NTs to absorb visible light, non-metals such as C [16], N [17], and B [18] have recently been

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doped into TiO<sub>2</sub> and proved significant enhancements in visible light photoactivities. For examples, Wang and his colleagues [19] successfully prepared C doped TiO<sub>2</sub> NTs by thermal treatment at 550 °C, and the doped photocatalyst showed 3.6 folds higher photocatalytic decomposition efficiency than that of TiO<sub>2</sub> NTs without doping. Liu et al. [20] investigated the visible absorption capacity, photocurrent response and photocatalytic activity of N-doped TiO<sub>2</sub> NTs, and the N doping significantly improved the photoelectrochemical properties. Furthermore, Peng and his co-workers [21] prepared B and N codoped TiO<sub>2</sub> NTs, and the samples exhibited excellent photoelectrochemical properties and photocatalytic activities under visible light irradiation. The previous results indicated that the TiO<sub>2</sub> NTs doped by nonmetal ions showed a significant improvement of optical and photoelectrochemical properties in applications of solar cells and organic pollutant degradation. However, these nonmetal ions in TiO<sub>2</sub> crystal lattices were easily destroyed at high temperature. The transition-metal-doped TiO<sub>2</sub> NTs are highly visible-active and stable, and many investigations about the preparation of TiO<sub>2</sub> NTs doped by transition-metal have been reported [22,23]. Fe<sup>3+</sup> ions were found to be significantly effective in enhancing TiO<sub>2</sub> photoelectrochemical activities under visible light irradiation. For examples, Prof. Sun [24] prepared Fe<sup>3+</sup> doped TiO<sub>2</sub> NTs by electrochemical anodic oxidation of pure titanium in HF electrolyte containing Fe<sup>3+</sup> ions, and the TiO<sub>2</sub> NTs-Fe showed an excellent photocatalytic removal efficiency of methylene blue (MB) dyes. Sun [25] and Sang [26] also successfully fabricated Fe-incorporated TiO<sub>2</sub> NTs with high visible-light-driven photocatalytic activities by ultrasound-assisted impregnating-calcination and template-based liquid phase deposition methods, respectively. The above results indicated the TiO<sub>2</sub> NTs doped by Fe<sup>3+</sup> ions could remarkably improve the visible light response, photocurrent and photocatalysis. However, these doping progresses by these methods are different to achieve or cause asymmetrical dopant concentrations at the surface. The solvothermal method provides a simple and environmental technique for the crystallization and doping due to high temperature and pressure in an enclosure space, and this method could achieve the uniform doping. To the best of our knowledge, little work has been reported so far concentrating on the solvothermal preparation of Fe<sup>3+</sup> doped TiO<sub>2</sub> NTs with high visible light activities.

In this article, we reported a facile solvothermal way to obtain highly visible light active Fe<sup>3+</sup> doped TiO<sub>2</sub> NTs exhibiting an exceptionally photoelectrochemical activity under solar light irradiation. It was proven that the prepared Fe-TiO<sub>2</sub> NTs film could significantly enhance the visible light absorption and photoelectrochemical activities as compared to those of TiO<sub>2</sub> NTs alone under same experimental conditions.

## 2. Experimental section

### 2.1. Materials

Titanium foil, ammonium fluoride (NH<sub>4</sub>F), ferric trichloride (FeCl<sub>3</sub>), sodium sulfide (Na<sub>2</sub>S), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), glycol and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All of the reagents were directly used without further treatment. Distilled water was used throughout our experiments.

### 2.2. Preparation of Fe<sup>3+</sup> doped TiO<sub>2</sub> NTs

TiO<sub>2</sub> NTs were prepared by a two-step anodization of Ti foils according to our previous reports [27]. The Fe<sup>3+</sup> doped TiO<sub>2</sub> NTs were synthesized by a solvothermal method in FeCl<sub>3</sub> solution with

different concentrations. In a brief, FeCl<sub>3</sub> with different amounts were dissolved in 30 ml of ethanol to obtain 0.5, 1 and 5 mmol/L Fe<sup>3+</sup> solution. Subsequently, the as-prepared TiO<sub>2</sub> NTs were immersed into Fe<sup>3+</sup> solution. Thereafter, the mixture solution was filled in Teflon-lined autoclave with 50 mL Teflon cup, and maintained at 180 °C for 14 h. After the solvothermal procedure, the resulting film was taken out and washed with ethanol for several times. The samples were dried at 60 °C for 6 h. The samples prepared in 0.5, 1 and 5 mmol/L Fe<sup>3+</sup> solution were marked as Fe-TiO<sub>2</sub> NTs (0.5), Fe-TiO<sub>2</sub> NTs (1) and Fe-TiO<sub>2</sub> NTs (5), respectively.

### 2.3. Characterization

The structure and composition of samples were studied by X-ray diffraction (XRD) using a German Bruker D8 X-ray diffractometer with the K $\alpha$  radiation of Cu ( $\lambda = 0.15418$  nm). The morphology was characterized by scanning electron microscopy (SEM) using a Hitachi S4800 equipped with X-ray energy dispersive spectroscopy (EDS) capabilities. X-ray photoelectron spectroscopy (XPS) was performed on AMICUS, Kratos Analytical (Shimadzu group company), using monochromatic source Mg K $\alpha$  (1253.6 eV). UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded with a Hitachi U-3010 spectrometer equipped with a 60 mm diameter integrating sphere using BaSO<sub>4</sub> as the reflectance sample.

### 2.4. Photoelectrochemical performance measurements

The photocurrent measurements were performed using a classical three-electrode cell consisting of Fe-TiO<sub>2</sub> NTs as the photoelectrode (working electrode), Pt counter electrode and a saturated calomel reference electrode. The photocurrent response was recorded on a CHI 620E electrochemical workstation using 0.1 M Na<sub>2</sub>S and 0.1 M Na<sub>2</sub>SO<sub>3</sub> as the electrolyte solution. The working electrode was irradiated by a 500 W Xenon lamp with a 400 nm long pass filter.

The photoelectrocatalytic (PEC) properties of Fe-TiO<sub>2</sub> NTs were evaluated by the removal of MB and Cr(VI) in aqueous solution under irradiation of solar light simulated by 500 W Xenon lamp (CEL-S500, China) in a homemade photoreactor. A 0.1 M K<sub>2</sub>SO<sub>4</sub> solution was used as supporting electrolyte, and the potential was fixed at 1 V. After stirring for 30 min in dark to achieve adsorption equilibrium, the reaction was conducted by magnetic stirring. After solar-light irradiation for 20 min, the remaining dye concentration was determined with a UV 1700 UV–vis spectrophotometer by detecting the maximum absorption wavelength for MB at 664 nm.

The PEC removal of Cr(VI) was similarly performed with the PEC degradation of MB. A 0.1 M NaCl solution was used as supporting electrolyte, and the potential was fixed at 0.5 V. The Cr(VI) concentration was determined colorimetrically at 540 nm using the diphenylcarbazide method.

## 3. Results and discussion

The powder XRD patterns of TiO<sub>2</sub> NTs and Fe-TiO<sub>2</sub> NTs (1) are shown in Fig. 1. The XRD peaks at 35.1°, 40.2° and 53.0° can be assigned to titanium substrates. The peaks at 25.3°, 36.9°, 37.8°, 38.6°, 48.0°, 53.9° and 55.1° are from (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5) and (2 1 1) diffractions of anatase-phase TiO<sub>2</sub> (JCPDS No. 21-1272). Additionally, these diffraction peaks of TiO<sub>2</sub> NTs still present after solvothermal doping progress without any impurities of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, but show small deviates toward small angles. The deviates could be attributed to lattice expansion caused by the dopant of Fe<sup>3+</sup> into TiO<sub>2</sub> crystal lattices. The substitution of Fe<sup>3+</sup> ions in TiO<sub>2</sub> crystal lattices causes the crystal expansion of lattice distances, which could explain the left-shift of these diffraction

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