

# $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ti–Nb–Zr–O composite photoanode for enhanced photoelectrochemical water splitting



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## ABSTRACT

Surface modification and doping of titanium dioxide (TiO<sub>2</sub>) nanotubes are efficient ways to obtain improved photosensitive characteristics. Here we report photocatalytic activity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> decorated Ti–Nb–Zr–O nanotube arrays. The Ti–Nb–Zr–O nanotube arrays were fabricated through anodization of Ti–Nb–Zr alloy in electrolytes of 1 M NaH<sub>2</sub>PO<sub>4</sub> containing 0.5 wt% HF. X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the heterojunction nanofilms. Nb- and Zr-doping could enhance the photocatalytic properties of the titanium oxide. However, more Zr-doping could lead to many defects that acted as recombination centers, which reduced the photocatalytic activity of the titanium oxide. The photocurrent density of the Ti–Nb–Zr–O nanotube photoanodes decorated with a small quantity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> could exhibit three times as high as that of the undoped TiO<sub>2</sub> nanotube photoanodes.

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## 1. Introduction

With the continuous reduction of fossil fuels, many researchers have devoted to seek new sources of clean energy. Since Fujishima and Honda reported on photoelectrochemical (PEC) water splitting at semiconductor electrodes in 1972, TiO<sub>2</sub> has emerged as a promising material for photocatalytic hydrogen production [1–3]. However, TiO<sub>2</sub>-based photoanodes usually have two major problems: (1) the wide band gap (3.2 eV) of TiO<sub>2</sub> limits the application on PEC water splitting, (2) fast recombination of excitons due to the short diffusion paths of charge carriers [4,5]. In order to improve the catalytic activity of TiO<sub>2</sub>, many elements (Fe, Mo, Cr, B, C, N, S and F) have been used to dope TiO<sub>2</sub> [6–12]. Recently, one dimensional nanotubular structures have aroused great interests mainly due to their high surface area and easily functionalized architecture with vectorial electro percolation pathways to reduce the recombination of electron [13]. Electrochemical anodization was an effective method to fabricate doped TiO<sub>2</sub> nanotubes. Ding et al. [14] fabricated Nb-doped TiO<sub>2</sub> nanotubes through the anodization of Ti–Nb alloys. Mohapatra et al. [15] reported the fabrication of Ti–Mn–O nanotube arrays via the anodic oxidation of Ti<sub>8</sub>Mn alloys.

Although the strategy of doping has led to some promising results, catalytic effect of the doped titanium oxide did not improve greatly. The modification of TiO<sub>2</sub> with other small band gap semiconductors such as Cu<sub>2</sub>O, WO<sub>3</sub>, CdS, CdTe and PbS has been employed to enhance the efficiency of photocatalytic water splitting [16–20]. Hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has been explored as water splitting photoanode. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> could absorb and utilize about 40% of the incident solar spectra because of its small band gap (approximately 2.2 eV). With good stability and absorption in the visible region the hematite iron oxide has been considered as potential candidate for the PEC system [21–25].

To date, rare work has been reported on the photocatalytic properties of hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) decorated Ti–Nb–Zr–O nanotube arrays. In the present work, Zr-doped Ti–Nb–O nanotube arrays were prepared via electrochemical anodization. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ti–Nb–Zr–O composite photoanode was fabricated by spin coating. The effects of Zr content and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> decoration on the microstructures and photocatalytic properties of the Ti–Nb–Zr–O nanotube arrays were investigated.

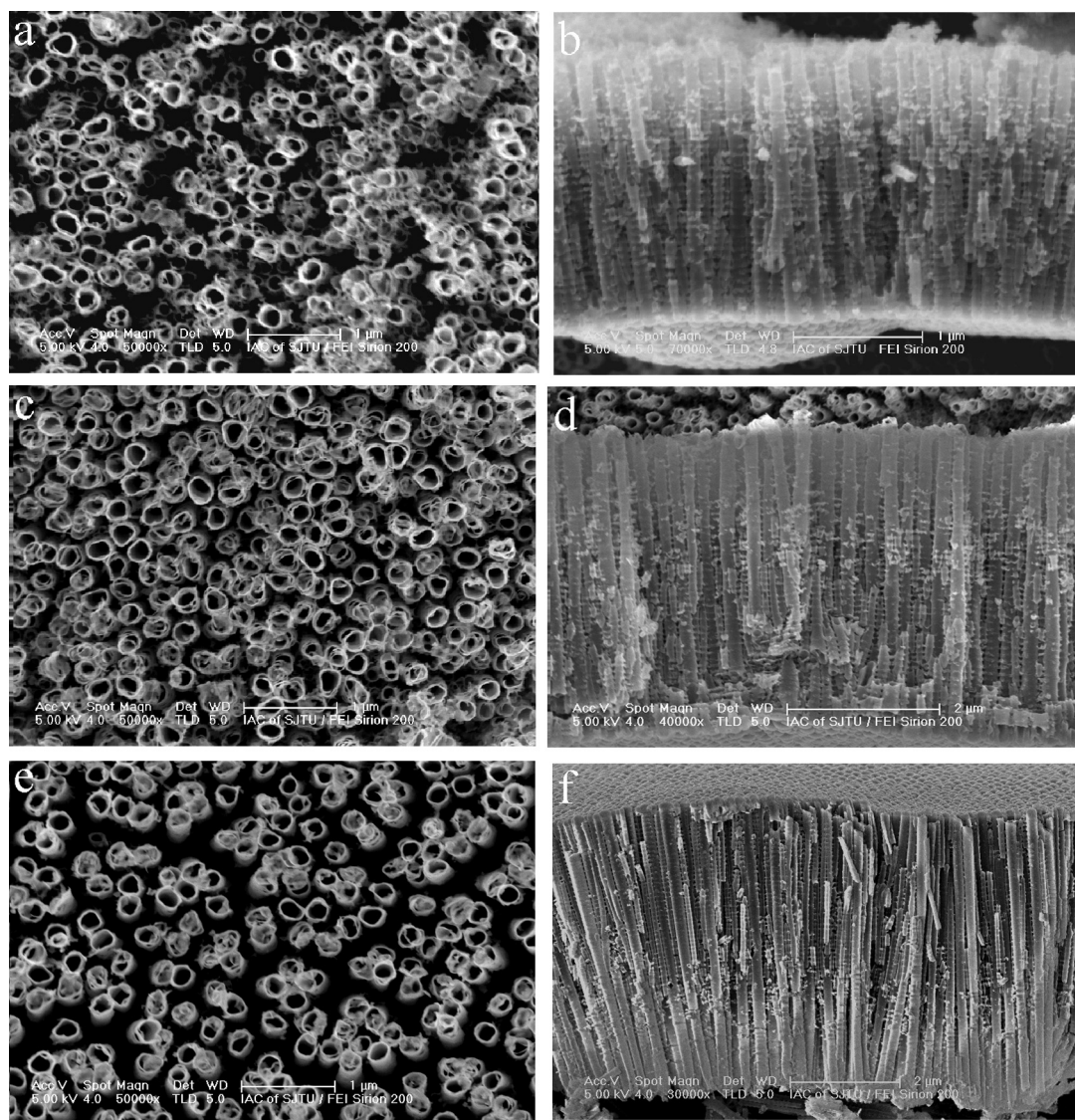
## 2. Experimental

### 2.1. Synthesis of Ti–Nb–Zr–O nanotube arrays

Plate samples of Ti<sub>35</sub>Nb (Ti-35 wt%Nb), Ti<sub>35</sub>Nb<sub>5</sub>Zr (Ti-35 wt% Nb-5 wt%Zr) and Ti<sub>35</sub>Nb<sub>10</sub>Zr (Ti-35 wt% Nb-10 wt%Zr) alloys were

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**Fig. 1.** Top and cross-section views of the nanotube arrays grown on different alloy substrates. (a) and (b)  $\text{Ti}_{35}\text{Nb}$ ; (c) and (d)  $\text{Ti}_{35}\text{Nb}_5\text{Zr}$ ; (e) and (f)  $\text{Ti}_{35}\text{Nb}_{10}\text{Zr}$ .

cleaned with absolute alcohol and deionized water before anodization. All the alloys used in the experiments were made in our laboratory (Ti–Nb–Zr alloys were fabricated using pure Ti plate, Zr plate and Nb–50%Ti alloys plate as raw material. Different quantity of Ti plate, Zr plate and Nb–50%Ti alloys plate were used to fabricate the Ti–Nb–Zr alloys according to Ti–Nb–Zr alloys component. The alloys were fabricated by the medium frequency induction furnace. The vacuum degree of cavity was pumped to lower than  $5 \times 10^{-3}$  Pa. And then the furnace was filled with argon (99.999%) and the pressure was kept at 50 MPa. The melting current was controlled at 350 mA to make all the metals melt uniformly. The as-fabricated casting was annealed at 1273 K for 36 ks and then solution treatment at 1123 K for 4 ks. Then the casting was quenched in water. Finally, the casting was made to Ti–Nb–Zr alloys plate for experiments through cold rolling technique). The anodization was performed in a two-electrode electrochemical cell with the Ti–Nb–Zr alloy as the working electrode and platinum foil as the counter electrode. Anodic samples were fabricated under a pulse voltage of 40 V with a constant frequency of 4000 Hz and duty cycle of 20% for 90 min in electrolytes of 1 M  $\text{NaH}_2\text{PO}_4$  containing 0.5 wt% HF. The temperature of the anodization bath was about 30 °C. After anodization, the samples were rinsed thoroughly with DI water

and then dried under a stream of nitrogen. The anodic samples fabricated with  $\text{Ti}_{35}\text{Nb}$ ,  $\text{Ti}_{35}\text{Nb}_5\text{Zr}$  and  $\text{Ti}_{35}\text{Nb}_{10}\text{Zr}$  alloy substrates were expressed as TN0Zr, TN5Zr and TN10Zr, respectively. The as-anodized samples were annealed at different temperatures (450 °C, 500 °C, 650 °C and 700 °C) for further investigation on photocatalytic properties.

## 2.2. Synthesis of $\alpha\text{-Fe}_2\text{O}_3/\text{Ti-Nb-Zr-O}$ composite structure

The  $\alpha\text{-Fe}_2\text{O}_3/\text{Ti-Nb-Zr-O}$  composite structure was fabricated by spin-coating method. Firstly, a precursor solution was prepared by dissolving 2.16 g  $\text{FeCl}_3$  in 200 ml ethylene glycol. Others literatures had reported the synthetic method of  $\alpha\text{-Fe}_2\text{O}_3$  [26]. The precursor solution was stirred for 4 h. The precursor solution was deposited on the Ti–Nb–Zr–O nanotubes by spin coating. The as-prepared films were subsequently heated on a hotplate in air at 350 °C for 5 min. The  $\beta\text{-FeOOH}/\text{Ti-Nb-Zr-O}$  composite structure was obtained after the heat treatment. This deposition and annealing procedure was denoted as one cycle. The film thickness was controlled by the number of cycle, rotation rate and time of spin coating. The rotation rate and time of spin coating were controlled at 3000 rpm and 40 s, respectively. The cycle number of the spin

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