



# Enhancing the photoelectrochemical water splitting activity of rutile nanorods by removal of surface hydroxyl groups



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## ABSTRACT

The effect of the surface hydroxyl (OH) groups on the photoelectrochemical (PEC) water splitting performance of rutile nanorod is examined. Based on the results of characterization, the surface OH groups are demonstrated to serve as the recombination centers for the photo-generated charges and to hinder the charge transfer at the interfaces. H<sub>2</sub>O<sub>2</sub> thermal and anneal treatments are applied to reduce the OH group surface coverage and both are proved effective. With reducing the relative surface OH coverage from 47 to 8%, the photocurrent density is increased from 0.419 to 0.642 mA cm<sup>-2</sup> at 0 V (vs. Ag/AgCl), achieving 53.2% improvement. Compared with the thermal treatment, H<sub>2</sub>O<sub>2</sub> treatment is more effective and energy-efficient. This work highlights that the surface property of the material itself is an important factor in the design of the PEC electrodes for water splitting.

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## 1. Introduction

TiO<sub>2</sub> photoanode has been intensively investigated for photoelectrochemical (PEC) water splitting because of its high chemical stability, nontoxicity, and low cost [1,2]. PEC water splitting includes charge transfer steps across the semiconductor/semiconductor and semiconductor/aqueous interfaces, and surface reaction steps, which involves charge transfer and reaction. Therefore, the efficiencies of photo-generated charge separation and transfer between the interfaces are the key factors deciding the overall efficiency of the process [3–5]. Therefore, the surface modification techniques, such as co-catalysts loading and semiconductors combination, have been intensively investigated for TiO<sub>2</sub> to enhance the photo-generated charge separation and transfer in water splitting reaction. With respect to the surface property of TiO<sub>2</sub> itself, it has been known that the surface hydroxyl (OH) groups play an important role in the adsorption of O<sub>2</sub> and affect the overall water splitting activity [6]. Oosawa and Grätzel and Kobayakawa et al. [7–9] investigated the effect of the surface OH density on the photocatalytic O<sub>2</sub> evolution reaction over a rutile TiO<sub>2</sub> powder catalyst from AgNO<sub>3</sub> solution. Oosawa and Grätzel [7,8] found that the O<sub>2</sub> generation activity is inversely proportional to the density of the surface OH groups. Kobayakawa et al. [9] reported that the O<sub>2</sub>

generation activity achieved a maximum under an optimal surface OH density. In these works, the authors ascribed the effect of the OH groups to the facilitated charge recombination on the surface OH sites. Though more direct and quantitative evidence is needed, these works show the importance of the material surface property in the design of the photocatalysts for water splitting.

Recently, many works focused on one-dimensional nanostructures, because of the improvement in charge carriers separation and transport on such materials [10–13]. In 2009, Liu and Aydil [14] reported a hydrothermal growth preparation method for the oriented single-crystalline rutile TiO<sub>2</sub> nanorods on fluorine-doped tin oxide (FTO) substrate, since then many works to enhance the PEC water splitting activity utilizing the rutile nanorods have been published, e.g. CdS and Cu<sub>2</sub>S quantum dots-sensitization, CdS/CdSe and In<sub>2</sub>S<sub>3</sub>/AgInS<sub>2</sub> co-sensitization, as well as the branched and three-dimensional hierarchical nanostructures utilizations [15–20]. It is noted that in the previous reports on the effects of the surface OH groups, rutile powder was dispersed in the solution and was utilized for the O<sub>2</sub> evolution reaction. The understanding on the effect of surface OH groups on the PEC water splitting activity of the nanorods is meaningful. With respect to the removal of the surface OH groups, anneal treatment was practiced, which requires high temperature and is accompanied with the risks of phase transformation and sintering. H<sub>2</sub>O<sub>2</sub> treatment is recently used for the catalytic material surface modification.

In this work, rutile TiO<sub>2</sub> nanorods are used as the photoanode material for PEC water splitting. The role of the surface OH groups

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on the catalytic performance in terms of the separation and transfer of the photo-generated electrons and holes is elucidated.  $\text{H}_2\text{O}_2$  treatment (HTT) is utilized as a tool to monitor the coverage of the surface OH group. As comparison, a regular anneal treatment (AT) is also discussed.

## 2. Material and methods

### 2.1. Preparation of rutile nanorod photoanode

Rutile nanorods were directly grown on a FTO substrate with a hydrothermal process [14]. Hydrochloric acid (37% by weight), titanium butoxide (AR, Tianjin Guangfu Technology Development Co., Ltd) were used as the raw materials. In a typical synthesis, two pieces of FTO substrates ( $3 \times 3 \text{ cm}^2$ ), which had been ultrasonically cleaned for 30 min in a mixed solution of deionized water, acetone and 2-propanol with volume ratios of 1:1:1, were placed at an angle against the wall of a teflon lined (100 mL volume) stainless steel autoclave with the conductive side facing down. Deionized water (30 mL) and hydrochloric acid (30 mL) was mixed and ultrasonically stirred for 5 min, and then 1 mL of titanium butoxide was added. After another 5 min of ultrasonic stirring, the solution was transferred into the autoclave. Then the autoclave was sealed and maintained at  $180^\circ\text{C}$  for 4 h followed by natural cooling to room temperature. The as-grown samples were rinsed with deionized water and absolute ethanol, dried in ambient air, and then annealed at  $450^\circ\text{C}$  for 0.5 h to enhance the contact between the rutile nanorods and FTO layer. The electrode obtained after above steps is referred to as the raw sample.

### 2.2. Modification of surface coverage of hydroxyl groups

AT and HTT were carried out, respectively, to monitor the surface coverage of the OH groups. Samples after AT at  $450^\circ\text{C}$  for 1, 2, 3 and 4 h are referred to as AT-xh (AT, anneal treatment; x, treatment time). In HTT, a piece of raw sample was put into a 100 mL beaker at an angle against the wall with the conductive side facing down. After added 50 mL  $\text{H}_2\text{O}_2$  solution (30% by weight, Tianjin Guangfu Technology Development Co., Ltd) without further treatment, the beaker was placed into the water bath with the temperature maintained at  $80^\circ\text{C}$  for 0.5, 1, 1.5 and 2 h. Samples after HTT are referred to as HTT-xh (HTT,  $\text{H}_2\text{O}_2$  thermal treatment; x, treatment time). In addition,  $\text{H}_2\text{O}_2$  treatment was also carried out at  $25^\circ\text{C}$  for 0.5 and 1 h, and the samples after this are referred to as HNT-xh.

### 2.3. Characterization

The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance X-ray Diffractometer with Cu  $\text{K}\alpha$  radiation. The surface morphology was observed with a Hitachi S-4800 field-emission scanning electron microscope (SEM). The high-resolution transmission electron microscopy (HR-TEM) analysis was carried out with a JEOL JEM-2100F instrument. The UV–vis absorption spectra of the samples were acquired with an UV–vis spectrometer (PerkinElmer, Lambda 750S). The Photoluminescence (PL) spectra were obtained with Jobin Yvon Fluorolog 3-21 in 1 M NaOH solution to identify the photo-generated charges separation and utilization efficiency. The surface properties of the prepared samples were characterized by X-ray photoelectron spectroscopy (XPS, Perkinelmer, PHI1600 ESCA).

### 2.4. Photoelectrochemical water splitting measurements

The photocurrent density ( $J$ )–potential ( $V$ ) and chopped  $J$ –time ( $t$ ) curves were obtained with a three-electrode setup, in which we used rutile nanorods as the working, Pt gauze as the counter,

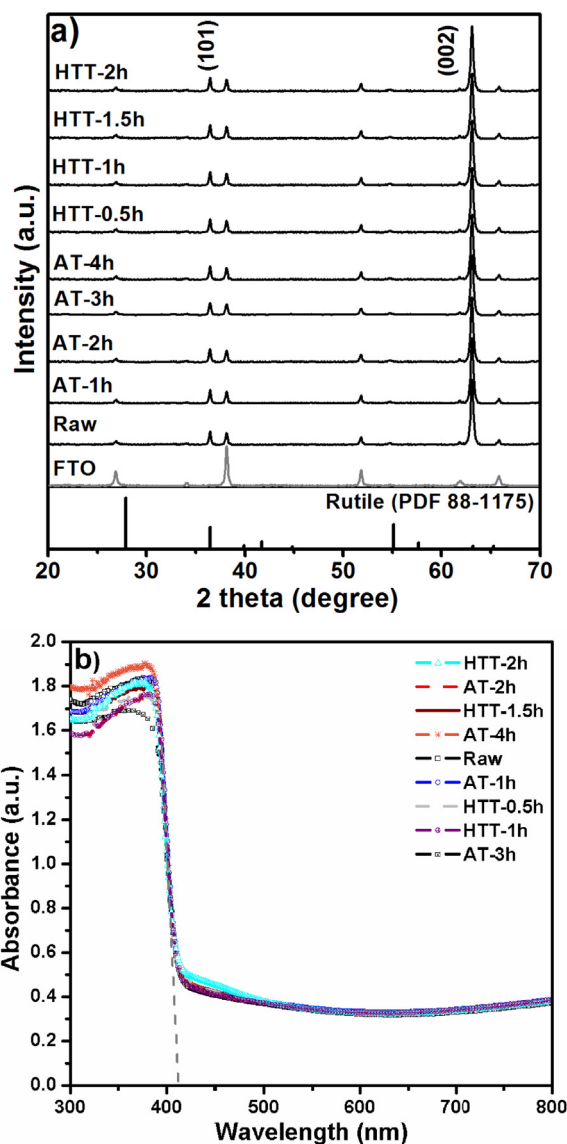


Fig. 1. (a) X-ray diffraction patterns of the bare FTO substrate and rutile nanorods arrays with/without surface modifications, (b) UV–vis light absorption spectra of the raw sample, HTT-xh and AT-xh samples.

Ag/AgCl as the reference electrodes, and 1 M NaOH solution as the electrolyte. A 300 W Xe-lamp (Perfect Light, PLS-SXE-300) coupled with an AM 1.5G filter was applied as the light source. By changing the applied lamp current and the distance between the lamp and the rutile nanorods photoanode, the illumination intensity was adjusted to  $100 \text{ mW cm}^{-2}$ . The PEC data were measured using a Princeton Applied Research Versa STAT3 Potentiostat. The  $J$ – $V$  curves were obtained with a scan rate of  $5 \text{ mV s}^{-1}$ , and the chopped  $J$ – $t$  curves were obtained at an applied potential of 0 V (vs. Ag/AgCl). Electrochemical impedance spectroscopy (EIS) was measured with applying a 10 mV AC signal within a frequency range from 0.5 Hz to 100 kHz at the open-circuit potential of the PEC cells.

## 3. Results and discussion

Fig. 1a displays the XRD patterns of the bare FTO substrate and rutile nanorods grown on FTO. The diffraction peaks of the grown samples agree well with the tetragonal rutile phase (PDF no. 88–1175), and the (101) and (002) planes can be assigned. The (002) diffraction peak appears as the most intense one,

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