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Photoelectrical and charge transfer properties of hydrogen-evolving TiO₂ nanotube arrays electrodes annealed in different gases

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ABSTRACT

TiO₂ nanotube arrays were fabricated by sonoelectrochemical anodic oxidation and calcined in nitrogen, air, or 5% hydrogen/nitrogen which was denoted as TNT-A, TNT-N, and TNT-H, respectively. All annealed TiO₂ nanotube arrays samples exhibited similar surface morphology. With UV illumination (365 ± 15 nm), the photocurrent density of the TNT-A, TNT-N and TNT-H was about 0.27 mA/cm², 0.45 mA/cm² and 0.60 mA/cm², respectively. The trapped electron at the Ti⁴⁺ center of TiO₂ nanotube arrays shows absorption at around 500–700 nm. From the XPS measurement, it was found that annealing in 5% hydrogen/nitrogen helped the sample obtain a greater defect density. Because of the reduction of Ti⁴⁺ and the formation of oxygen vacancies, the charge transfer resistance appeared in this order: TNT-A > TNT-N > TNT-H. Thus TNT-H harvested the greatest charge carrier density of 9.86 × 10²⁰ cm⁻³, TNT-N and TNT-A obtained a charge carrier density of 1.38 × 10²⁰ cm⁻³ and 1.06 × 10²⁰ cm⁻³, respectively. Accordingly, the hydrogen production rate by water splitting over TNT-A, TNT-N and TNT-H (320–780 nm irradiation, 3 h) was about 120 μL/h cm², 159 μL/h cm² and 231 μL/h cm², respectively.

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1. Introduction

Hydrogen is an effective energy carrier, and a possible alternative vector to reduce the strong dependence on fossil fuels, particularly in the transportation sector, to help address the energy and environmental concerns [1,2]. Since Fujishima and Honda [3] proved that water can be photoelectrochemically cleaved into its constituents on n-TiO₂ electrode, many studies focused on this semiconductor photocatalysts for their applications to the water splitting reaction [4–9]. Recently, TiO₂ nanotube arrays attracted much attention in hydrogen production by water splitting because of their large

surface area and controllable surface properties [10–12]. In 2001, Grimes [13] successfully generated titanium dioxide nanotube arrays on titanium by anodic oxidation. The advantage of the anodization method is that TiO₂ nanotubes are readily attached onto a conductive substrate of titanium and form nanotubes oriented, aligned perpendicular to the substrate. In addition, the resulting oriented TiO₂ nanotube arrays film can be directly used as the working electrode in the photocatalytic reaction offering much better electron transfer pathways than non-oriented structures.

Defect disorder of the photoelectrode surface layer and the bulk phase are entirely different, leading to the formation of

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a potential barrier. This has a substantial effect on charge separation [14], which is one of the important factors for the efficiency of energy conversion. In the work described in this paper, we fabricated TiO₂ nanotube arrays via sonoelectrochemical anodization process and focused on investigating the charge transfer mechanism and the photoelectrical behaviors of the electrodes which were annealed in oxygenous gas (air), anaerobic gas (N₂) and reducing gas (5% H₂/N₂), respectively. The experimental results revealed that the appropriate defect disorder could be obtained by annealing in reducing gas, which can help to increase the photoelectrical and charge transfer properties.

2. Experimental

2.1. Materials

Titanium foils (0.2 mm thick, 99.6% purity) were supplied by STREM CHEMICAL. Phosphate acid (H₃PO₄ ≥ 85%), sodium fluoride (AR) was purchased from Tianjin Chemical Reagent Company. Ethanol (AR), potassium hydroxide (AR) and acetone (AR) were purchased from Beijing chemical works. All solutions were prepared using high-purity DI water.

2.2. Preparation of TiO₂ nanotube arrays

During a fabrication process of TiO₂ nanotube arrays film, titanium foil, was cut into samples of size 65 mm × 18 mm, were degreased by ultrasonic waves in acetone, then washed in the ethanol and high-purity DI water, and dried in air. Electrochemical anodization of titanium used DC power (LWDQGS, 0–3 A, 0–60 V) to supply 20 V DC voltage. The anodization experiments [15] were carried out under ultrasonication (Kunshan Ultrasonic Instrument Co., Ltd. KQ-100DE) at room temperature for 1 h using a platinum sheet (50 mm × 5 mm) counter electrode. 0.5 M phosphoric acid and 0.14 M sodium fluoride solution used for electrolytic solution. All the obtained samples were thoroughly rinsed with high-purity DI water. Then the as-grown TiO₂ nanotube arrays were annealed at 500 °C in tube furnace, under a flow of reducing gas (5% H₂/N₂) with a heating rate of 5 °C/min and dwelled 4 h, and cooled to room temperature under a continuous 5% H₂/N₂ flow. The as-grown TiO₂ nanotube arrays also were annealed in oxygenous gas (air) or anaerobic gas (N₂) under the same conditions. The sample annealed in air, N₂ or 5% H₂/N₂ was denoted as TNT-A, TNT-N and TNT-H, respectively.

2.3. Characterization of TiO₂ nanotube arrays electrode

The surface morphology of the as-prepared titanium dioxide film was characterized with a field emission scanning electron microscope (Hitachi, Japan, S4300). The crystal structures of the samples were determined using an X-ray diffraction meter (D8 ADVANCE BRUKER/AXS). The surface composition of the TiO₂ nanotube arrays was analyzed with an X-ray photoelectron spectroscope (XPS, ThermoFisher Scientific ESCALAB 250). The optical absorption spectra were obtained using a diffuse reflectance ultraviolet and visible spectrophotometer (Shimadzu, Japan, UV-2450 with IRS-2200).

2.4. Photoelectrochemical activity and hydrogen generation measurements

The photoelectrochemical (PEC) experiments were performed in a rectangular shaped quartz reactor (80 mm × 60 mm × 80 mm) using a three-electrode system with a platinum gauze (30 mm × 20 mm) counter electrode, a saturated Ag/AgCl reference electrode and a TiO₂ nanotubes work electrode (10 mm × 10 mm) in 1 M KOH. A 300 W Xe lamp with a filter (320 nm–780 nm) was used as a light source. The light passed through a 365 ± 15 nm filter was 12.7 mW/cm². All the data were collected by a CHI electrochemical analyzer (CHI 614C, CH Instruments, Inc.). The electrochemical photocell for hydrogen generation was a three-electrode configuration with three separate compartments connected by a 1 cm diameter fine glass frit. Detection of hydrogen was made online by using an Agilent 4890D gas-chromatograph (5 Å molecular sieve, Ar carrier gas).

3. Results and discussion

3.1. SEM and XRD analysis

Images in Fig. 1 show FESEM photographs of the top surface and cross section of the TiO₂ nanotube arrays which was fabricated by anodization for 1 h under ultrasonic waves and was annealed in air, N₂ and 5% N₂/H₂, respectively. Under the same anodization conditions, the nanotube arrays show a similar morphology, with the tube diameter of about 100 nm, wall thickness of about 15 nm and tube length of about 650 nm. The experimental results revealed that calcination in different gases did not affect the nanotubes morphology significantly.

Fig. 2 shows XRD patterns of the samples annealed at 500 °C for 4 h in air, N₂ and 5% H₂/N₂, respectively. As shown in Fig. 2, the annealed samples had single-phase anatase. It has been demonstrated that the barrier layer in TiO₂ nanotube arrays film mainly composed of rutile TiO₂ [16]. In these conditions, the resultant samples with the thin barrier layer, the diffraction peak intensity of rutile TiO₂ may be too weak to be detected. Fig. 2 also shows the different calcination atmosphere couldn't change the samples' crystal phase in the same calcination time.

3.2. Photoelectrochemical and charge transfer properties of TiO₂ nanotube arrays electrode

The UV–Vis diffuse reflectance spectra of the samples are shown in Fig. 3. It can be seen from Fig. 3 that the samples annealed in different gases exhibited the similar absorptions in 350–380 nm region. TNT-N and TNT-H had obvious absorption peak in visible region of 400–700 nm. Generally, the trapped hole exhibits the absorption at wavelength about 430 nm or even shorter, while the trapped electron at the Ti⁴⁺ center shows another absorption at around 500–700 nm for TiO₂ nanotube arrays [17]. In the 5% H₂/N₂ atmosphere, some Ti⁴⁺ in TiO₂ nanotube arrays was reduced to Ti³⁺. The high density of Ti³⁺ dopant states lead to the reduction of the sub-band gap to approx. 2.4 eV [18]. TNT-A exhibited an absorption

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