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Full Length Article

Facile fabrication of Si-doped TiO_2 nanotubes photoanode for enhanced photoelectrochemical hydrogen generation

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ABSTRACT

Photoelectrochemical (PEC) water splitting based doping modified one dimensional (1D) titanium dioxide (TiO_2) nanostructures provide an efficient method for hydrogen generation. Here we first successfully fabricated 1D Si-doped TiO_2 (Ti-Si-O) nanotube arrays through anodizing Ti-Si alloys with different Si amount, and reported the PEC properties for water splitting. The Ti-Si-O nanotube arrays fabricated on Ti-5 wt.% Si alloy and annealed at 600 °C possess higher PEC activity, yielding a higher photocurrent density of 0.83 mA/cm^2 at 0 V *vs.* Ag/AgCl. The maximum photoconversion efficiency was 0.54%, which was 2.7 times the photoconversion efficiency of undoped TiO_2.

1. Introduction

Photoelectrochemical (PEC) water splitting hydrogen evolution reaction (HER) is one of the important promising methods for low-cost and clean hydrogen production [1]. Since the pioneering works of Fujishima [2], TiO_2 has become one of the best photocatalysts due to its unique photoelectric and stable chemical properties [3,4]. However, the wide band gap and easy recombination of photo-generated carries make it could only absorb in the ultraviolet region of solar energy and this lead to lower quantum yields [5]. In order to address these main drawbacks, various modifications such as metal doping [6–8] and nonmetal doping [9–12], narrow semiconductor coupling [13–15], noble metal deposition [16,17], quantum dot [18,19] and dye sensitizing [20,21] were employed by researchers.

In recent years, one-dimensional (1D) TiO_2 nanotubes has been widely used in the fields of photocatalysis, dye-sensitized solar cells and biomedical devices, due to its large surface areas and good electron transport ability [22,23]. Meanwhile, Si element has been expected to be an ideal dopant for TiO_2, which could improve the thermal stability and possess fewer carrier recombination centers [3]. Very recently, Oh et al. synthesized Si-doped TiO_2 nanopowders by thermal plasma and investigated the effect of Si-doping content on photocatalytic activity [24]. Su et al. fabricated Si-doped TiO_2 nanotube arrays by anodizing Ti sheet with one-step chemical vapor deposition (CVD) treatment and obtained better PEC capability [25]. Jin et al. prepared Si-doped TiO_2 photocatalysts by hydrothermal process and pointed that Si doping contribute to the photocatalytic reduction efficiency of NO [26]. Zhang et al. synthesized Si-doped TiO_2 nanotubes with higher photocatalytic activity by anodizing Ti in HF/Na_2SiF_6 solution, and proved that Si doping facilitate for the separation of photo-generated electrons and holes [27]. Sun et al. invented the "solid-state oxide bath" method to prepare Si-doped TiO_2 thin film and obtained enhanced visible light PEC response [28]. To our knowledge, rare works have been reported on 1D Si-doped TiO_2 nanotubes fabricated on Ti-Si alloy and reported the relevant PEC properties.

Based on above analysis, we fabricated Ti-Si-O nanotubes by anodizing Ti-Si alloys with different Si content. The influences of Si-doping contents and annealing temperatures on PEC activity of Ti-Si-O nanotubes photoanodes were discussed. The Ti-Si-O nanotubes fabricated by anodizing Ti-5 wt.% Si alloy and annealed at 600 °C possess higher PEC activity compared with undoped TiO_2. Combined with microstructure analysis, optical property characterization and PEC measurements, the underlying mechanism for improvement on PEC performance of Ti-Si-O nanotubes photoanode was discussed. We believe the combination of unique 1D TiO_2

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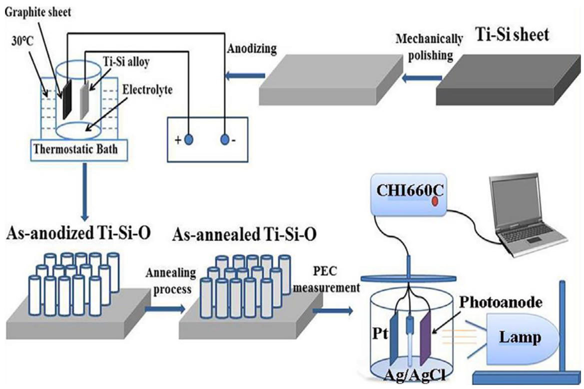

Fig. 1. Schematic diagrams of the fabrication process for Ti—Si—O nanotube arrays and the measurement setup for PEC water splitting.

nanotubes structure and moderate Si doping design will provide an efficient method for improving PEC performance of TiO_2-based photoanodes.

2. Experimental section

2.1. Preparation of Ti-Si-O nanotubes photanodes

Ti-Si alloys with different Si contents were casted by vacuum arc remelting (VAR) process. The raw materials were pure Ti and pure Si with purity of 99.99 wt.%. After melting, the ingots were cut by wire electric discharge machine into plate samples with a desired dimension (20 mm × 10 mm × 1 mm). The average Si content (wt.%) was 4.6 in the Ti-5 wt.% Si alloy and 8.3 in the Ti-8.5 wt.% Si alloy according to our X-Ray Fluorescence (XRF) analysis. X-ray diffraction (XRD) measurement showed that Ti_5Si_3 phase existed in Ti-Si alloys.

The schematic diagram of the fabrication process of Ti-Si-O nanotube arrays was shown in Fig. 1. Plate samples of the Ti-Si (Ti-5 wt.% Si and Ti-8.5 wt.% Si) alloys as well as pure Ti (for reference) were first mechanically polished with various types SiC emery papers, and then successively ultrasonic cleaned using acetone, absolute ethyl alcohol and deionized water. After then, the Ti-Si alloys were anodized in a two-electrode electrochemical cell, with graphite sheet as the counter electrode. Anodic samples were fabricated at a pulse voltage of 40 V for 20 min, with a 4000 Hz constant

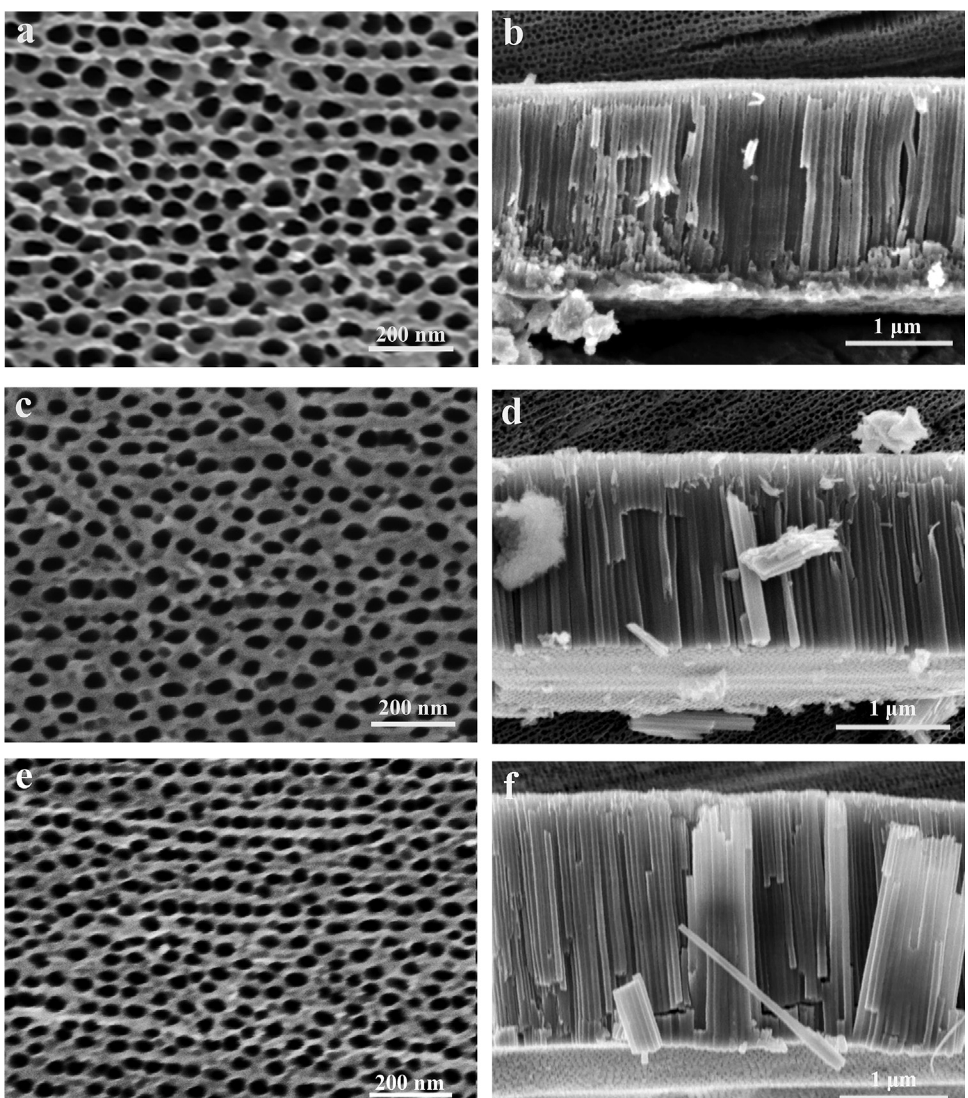

Fig. 2. Surface and cross-section view SEM images of the different Ti—Si—O nanotubes. (a-b) Ti0SiO; (c and d) Ti5SiO; (e and f) Ti8.5SiO. All of the samples were processed at 600 °C.