Nano Energy (2013) 2, 351–360

Available online at www.sciencedirect.com

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RAPID COMMUNICATION

Branched TiO_2/Si nanostructures for enhanced photoelectrochemical water splitting

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Received 28 August 2012; received in revised form 29 October 2012; accepted 30 October 2012
Available online 6 November 2012

KEYWORDS
Branched nanowires (b-NWs);
Heterojunction photoanode;
Photoelectrochemical cells (PECs);
Solar water splitting

Abstract
We report a successful fabrication of hierarchical three-dimensionally branched TiO_2/Si nanowire arrays and their application as the photoelectrochemical electrode for solar water splitting. The branched TiO_2/Si nanowire arrays improved the photoelectrochemical (PEC) performance compared to TiO_2 thin film-coated Si nanowire arrays because of the substantially increased surface area for electrochemical reactions and enhanced charge transfer kinetics. Wavelength-dependent photocurrent response of the branched nanowire array indicates a strong response in the ultraviolet region ($<$400 nm), while a negligible photocurrent is observed under visible illumination, primarily caused by the high overpotential loss of n-Si photoanode and energy band configuration of the TiO_2/Si heterojunction. The working mechanism based on recombination at this heterogeneous n–n junction is proposed. This study provides insights on the fundamental understanding and potential optimizations of nanoscale hierarchical 3D structured devices for renewable energy applications.
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Introduction

Since the first practical demonstration of photoelectrochemical (PEC) water splitting using a TiO_2-based photocatalyst [1], research efforts have been focused on various semiconducting materials and structures for efficient light harvesting, high quantum efficiency, enhanced PEC water

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2211-2855/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.nanoen.2012.10.010

splitting performance, as well as practical durability and low-cost manufacturing [2–10]. In particular, photoelectrodes based on dimension-controllable and highly ordered metal oxide nanostructure array [6,8,11–13] have attracted much attention for PEC applications. Such nanostructures offer a unique combination of the large surface areas/reaction sites, increased optical path lengths and thus low reflection, direct electronic carrier transport pathways, and short lateral diffusion length due to their one-dimensional (1D) nanostructures. Additional advantages such as superior chemical stability, ease of fabrication, and relative low cost inherited from oxide materials have also been noted. However, most metal oxides such as TiO_2, ZnO, and WO_3 have wide bandgaps, leading to a limited light absorption in the visible region of solar spectrum, unfavorable band positions with respect to the water oxidation and reduction levels, low electron mobility, and rapid electron–hole pair recombination [5]. To resolve these issues of metal oxide photoelectrodes, various investigations have been performed on metal/cation/anion doping, dye/quantum dot sensitization, metal ion-implantation, and heterojuction [14–17]. Among the aforementioned techniques, the heterojunction electrode approach utilizes two different semiconductors that form a heterojunction allowing enhanced light absorption and charge collection efficiency, which can also take advantage of electrochemically robust materials to improve photocorrosion stability [18–23].

Si is the most important and broadly used semiconductor in electronic and optoelectronic devices, which is also abundant and generally of low cost. Si is a desirable photoelectrode material for PEC applications because it has a narrow band gap, absorbs light efficiently, and has easily controllable electrical conductivity [3,24,25]. However, Si has poor chemical stability because it is rapidly oxidized in aqueous solution under solar illumination or under anodic bias [26]. On the other hand, TiO_2 has been extensively studied as photoanode material due to its superior chemical stability as well as photochemical and photocatalytic properties [7,27,28]. However, it absorbs sunlight only in the UV region and collects less than 5% of the total energy available in the solar spectrum [5,12] and thus offers a limited PEC performance. Therefore, a heterogeneous integration of Si and TiO_2 could combine their advantageous properties for PEC with good chemical stability and efficient light absorption.

Compared to a planar structure, a vertically oriented nanowire (NW) array exhibits a significant advantage of enhanced light absorption and energy conversion efficiency due to the following reasons [3,29–32]. First, vertically oriented NW array provides a reduced reflection and thus an enhanced sunlight absorption due to their light trapping properties. Second, the aligned NWs can orthogonalize the light absorption and the carrier collection processes due to the reduced competition between photon absorption and carrier collection, and short diffusion length of minority carriers. Third, the NWs also provide a larger internal surface area and reaction sites to improve the charge transfer and PEC reaction kinetics. In this regard, the core/shell NW (cs-NW) and three-dimensional (3D) branched NW (b-NW) heterostructures are very attractive photoelectrodes. Such structures offer combined advantages of heterojunction and 1D nanostructures [10,33,34]. The 3D b-NW heterostructures could offer greatly increased surface area and more enhanced light absorption in NW branches compared to the cs-NW heterostructures.

In this article, we report a successful fabrication of three-dimensional (3D) TiO_2/Si based branched NW arrays by a combination of nanoimprint lithography (NIL), reactive ion etching (RIE), and hydrothermal reactions. The b-NW structures were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), and X-ray diffraction (XRD). The TiO_2/Si b-NW arrays, in comparison with TiO_2/Si cs-NW arrays, with various Si NW lengths were studied as photoanodes for PEC water splitting. A working mechanism based on charge transfer and recombination at the n–n TiO_2/Si heterojunction is proposed.

Experimental

Fabrication of core/shell and branched TiO_2/Si NWs arrays

Fig. S1 in the Supporting materials shows a schematic diagram outlining the fabrication process of core/shell and branched TiO_2/Si NW arrays. First, vertical Si NW arrays were fabricated by combining nanoimprint lithography (NIL) and reactive ion etching (RIE) processes (see further details in the Supporting materials) [35–37]. To fabricate a TiO_2 thin film-coated Si NW (core/shell TiO_2/Si NW, cs-NW) array, a thin layer of TiO_2 was deposited on the Si NWs using RF magnetron sputtering (Denton Discovery, 18 Sputter System) at 400 W under 15 mTorr in an argon environment, and annealed at 400 °C for 30 min in nitrogen atmosphere. The TiO_2 thin film coating on Si NW surface serves as shells and also as a seeding layer for the growth of 3D branched TiO_2/Si NWs.

Branched TiO_2/Si NW (or TiO_2/Si b-NW) arrays were prepared by a hydrothermal reaction [38]. For hydrothermal processing solution, 1 ml of titanium *n*-butoxide (Alfa Aesar), the titanium precursor, was added drop-wise to a 1:1 mixture of DI water and concentrated hydrochloric acid (EMD chemicals) and stirred to obtain a clear transparent solution. The core/shell TiO_2/Si NW arrays were placed in the growth solution in a stainless steel autoclave with Teflon liner (Parr instrument), and then sealed and maintained at 155 °C for the growth of TiO_2 branches for various time periods. After the hydrothermal reaction, the samples were removed from the solution, rinsed with ethanol, and dried with nitrogen gas, and followed by annealing at 400 °C for 30 min in nitrogen atmosphere.

Characterization and measurements

A high-resolution scanning electron microscope (SEM, FEI XL30-SFEG) was employed to examine the NW morphology. The crystalline structures of TiO_2 NWs hydrothermally grown on Si substrate were further characterized by X-ray diffraction (XRD, Rigaku Multiflex X-ray diffractometer) with Cu-K_α radiation (λ = 1.54 Å) scanning at a rate of 0.05° s^{-1}. Transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-Twin) was carried out with 200 kV accelerating voltage (SINANO, China). For the TEM measurements, the TiO_2/Si b-NWs were scraped off from the substrate and dispersed in IPA using