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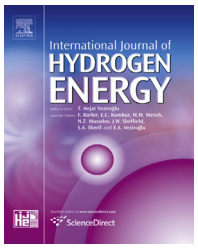

Irradiation-induced TiO_2 nanorods for photoelectrochemical hydrogen production

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ABSTRACT

In this work, well-ordered nanorods were fabricated on the surface of TiO_2 thin films deposited on Ti sheets by an ion irradiation method using nitrogen ion irradiation with the energy of 65 keV to a fluence of 1×10^{17} ions/cm^2. These TiO_2 nanorods are about 120 nm in length and 20–40 nm in diameter. After post-irradiation annealing at 500 °C in O_2, the nanorod array photoelectrode displays largely enhanced performance for photoelectrochemical (PEC) water splitting compared to that of the un-irradiated TiO_2 thin films with a planar structure. The influences of the irradiated ion energy on the morphology and photocurrent density of the nanorods were investigated. The 65 keV N^+ irradiated TiO_2 thin films shows a higher photocurrent density than those of the 45 and 85 keV N^+ irradiated TiO_2 thin films. We also discussed the influence of annealing conditions on the PEC performance of TiO_2 nanorods, and it was found that the nanorods annealed at 600 °C in vacuum produce a much higher photocurrent density of 0.6 mA/cm^2 at 0.8 V (vs. a saturated calomel electrode), which is about 7 times higher than that of the nanorods annealed in oxygen. This work proposes that ion irradiation combination with thermal annealing in vacuum could be an effective approach for developing nanostructured materials for water splitting.

Introduction

Since the first study of photoelectrochemical (PEC) water splitting on TiO_2 by Fujishima and Honda in 1972 [1], considerable efforts have been devoted to develop suitable photoelectrode materials in order to further improve the solar-to-hydrogen conversion efficiency. Among various photoelectrode materials, TiO_2 have been extensively

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investigated for PEC water splitting, due to their excellent properties such as their high resistance to photocorrosion, high chemical stability, nontoxicity, and low cost [1–3]. However, its wide band gap (3.2 eV) and the low quantum yield largely limit the overall water-splitting efficiency. To extend the optical absorbance band edge into the visible light range and prevent the recombination of electron–hole pairs, great efforts have been made by decorating titanium oxide with noble metal nanoparticles (NPs), ion doping, sensitizing with organic dyes, conducting polymer, or semiconductor quantum dots with narrow band gap [4–10], etc. The newly emerging nanotechnology offers another effective solution to improve the PEC performance of TiO_2. One-dimensional (1D) nanostructures, such as nanorods [11,12], nanotubes [13–16], and nanowires [17,18], which have smaller diffusion distance of carriers and larger surface areas, are expected to have improved charge separation, charge transport, and light absorption properties compared to TiO_2 thin films with a planar structure.

The methods to fabricate 1D TiO_2 nanostructures include colloidal synthesis [19,20], electrodeposition [21], organometallic chemical vapor deposition (OMCVD) [22,23], chemical vapor deposition (CVD) [24,25], oblique-angle deposition (OAD) [11], hydrothermal processes [26,27]. Besides, one unique method for the fabrication and tailoring of nanostructured materials is via ion beam modification [28]. The fabrication of nanostructures by ion irradiation results from the formation of atomic defects in the target and the spatial distribution of energy deposited by charged particles [29]. Compared to other methods for fabricating nanostructures, ion beam technique provides a simple way to produce nanostructures with controlled shape and size and has a good repeatability. Moreover, this technology, especially when combining with heat treatment to recover the damage, can also achieve beneficial effects on nanostructured materials induced by ion irradiation. Thus, ion beam synthesis of nanostructures has attracted much attention. The formation of nanopores after ion irradiation has extensively been reported in different types of semiconducting materials, such as germanium (Ge) [30], indium antimonide (InSb) [31], and gallium nitride (GaN) [32]. Ion beam technology is also an important technology for doping of semiconductor [33,34]. In our previous work, we fabricated TiO_2 nanorods on the TiO_2 surface by N^+ ion irradiation of single crystal bulk TiO_2 and the work demonstrated that ion irradiation may be a powerful method to tailor the surface nanostructure of TiO_2 [35]. The formed TiO_2 nanorods are expected to have promising photoelectrochemical properties for hydrogen generation by water splitting.

In this paper, we report the fabrication of well-order TiO_2 nanorods arrays on Ti sheets by N^+ ion irradiation of TiO_2 thin films. To prepare the photoelectrode for solar water splitting, TiO_2 thin films instead of bulk TiO_2 was used as the target material for ion irradiation. Under the same annealing conditions, the TiO_2 nanorod arrays working as the photoelectrode exhibit distinctly higher photocurrent density compared to that of the un-irradiated TiO_2 thin films. In order to achieve the optimized PEC performance, the influences of the irradiation ion energy, post-irradiation annealing temperature and annealing atmosphere on the photocurrent density of TiO_2 nanorod arrays were investigated. Our study has demonstrated ion irradiation combination with thermal annealing in vacuum is an effective approach for the fabrication of TiO_2 nanorods as a photoelectrode for efficient PEC water splitting devices.

Experimental

Sample preparation

Amorphous TiO_2 thin films with a thickness of ~200 nm were deposited on Ti slices by the atomic layer deposition (ALD) method. Ion irradiation was performed at room temperature with N^+ ions with energies of 45, 65 85 keV to the same fluence of 1×10^{17} ions/cm^2. Normal incidence of ions was carried out for the irradiation, and the samples were grounded. The mean projected ranges (Rp) for 45, 65, 85 keV were calculated to be 79, 110, and 142 nm, respectively, by the TRIM simulation [36]. The TiO_2 thin films irradiated by N^+ ions at 65 keV were annealed at 300 °C, 400 °C, and 500 °C for 2 h, and 600 °C for 30 min under flowing oxygen gas and at 600 °C for 30 min in vacuum. The TiO_2 thin films irradiated by N^+ ions at 45 and 85 keV were annealed at 400 °C for 2 h in oxygen. The un-irradiated TiO_2 thin films annealed at 500 °C for 2 h in oxygen were also prepared as a reference.

Characterization

The surface morphologies of all samples were examined using scanning electron microscopy (SEM, FEI Sirion). X-ray diffraction (XRD) patterns were measured on a PANalytical X'pert MPD Pro X-ray diffractometer using Cu Kα irradiation. X-ray photoelectron spectra (XPS) were recorded using a Thermo Scientific ESCALAB 250Xi system with an Al kα (1486.6 eV) source.

PEC measurements were carried out in a conventional three-electrode configuration, with a saturated calomel reference electrode, platinum plate counter electrode, and the TiO_2 films as the working electrode, in a quartz-windowed cell. We used 0.5 M Na_2SO_4 as the electrolyte. The illuminated surface areas of the working electrode were fixed at 0.785 cm^2. An electrochemical workstation (CHI660D) and a 500 W Xe lamp solar simulator with the illumination intensity of 100 mW/cm^2 adjusted through an AM 1.5G filter were used for photocurrent density–potential (I–V) measurements.

Results and discussion

The influence of irradiated ion energy on the photocurrent of TiO_2 nanorods

The original TiO_2 thin films deposited on Ti slices showed a very flat surface. After 65 keV N^+ ion irradiation, the nanorod surface structure was obtained (see Fig. 1(a)). These nanorods are aligned to be consistent with the incident angle of ion beam and normal to the substrate. Overall length of the nanorods was found to be fairly uniform and the mean length is about 120 nm. For individual nanorod, the diameter from