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V ions implanted ZnO nanorod arrays for photoelectrochemical water splitting under visible light

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ABSTRACT

In this work, V ions were doped into ZnO nanorod arrays via an advanced ion implantation method for photoelectrochemical water splitting under visible light. It was indicated that the V dopants were incorporated into ZnO lattice as V^{4+} and V^{5+} ions. V ion doping expanded the optical absorption of ZnO nanorod arrays into visible light region and led to considerable photoelectrochemical performance under visible light illumination ($\lambda > 420$ nm). The photocurrent density of V ions doped ZnO nanorod arrays could achieve 10.5 $\mu A/cm^2$ at 0.8 V (vs. Ag/AgCl), which was about 4 times higher than that of the pure ZnO nanorod arrays. The enhancement in photoelectrochemical performances for V ions doped ZnO nanorod arrays should be attributed to the improved visible light absorption ability and the increased charge carrier density induced by V ion doping.

Introduction

Zinc oxide (ZnO) has been widely investigated for solar water splitting because of its low cost, non-toxicity, chemical and thermal stability and appropriate conduction/valence band edges for water reduction and oxidation [1–6]. However, only ultraviolet (UV) light can be utilized for solar water splitting due to its wide band gap (3.37 eV). During the past years, to utilize the much more energy contained in the visible light region than in the UV region of the sunlight [7], continuous efforts have been made to activate ZnO under visible light, such as cation and anion doping [8,9], quantum dots sensitization [10] and composite semiconductor [11], etc.

Metal ion doping has been extensively investigated to be an effective method for modifying the electronic structure of wide band gap semiconductors and shifting its photoresponse to the visible light region. Various methods have been employed to dope metal ions into semiconductor, such as ion implantation [12], sol–gel [13], and hydrothermal method [14]. When transition metal ions are incorporated into the crystal lattice of ZnO, impurity energy levels will be formed in the forbidden band gap and hence narrow the band gap, which makes ZnO active in the visible light region for

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solar water splitting. For example, Shet et al. [15] prepared Al, N co-doped ZnO thin film by radio-frequency magnetron sputtering in mixed O_2 and N_2 atmosphere, which displayed a maximum photocurrent of about 12 μA/cm^2 at 1.0 V vs. Ag/AgCl under visible light irradiation. Yousefi et al. [16] synthesized Ce doped ZnO thin films by sol–gel method and anealed at 500 °C. Under visible light irradiation, Ce doped ZnO obtained maximum photocurrent of 1.2 μA/mm^2 at 1.2 V vs. Ag/AgCl. Recently, Shen et al. [17] successfully constructed a ZnO/ZnO:Cr isostructural nanojunction by a two-step electrodeposition process for photoelectrochemical (PEC) water splitting. The introduced intra-bandgap states associated with Cr impurities led to increased optical absorption and hence considerable PEC performance in visible light. All these studies demonstrated that metal ion doping could effectively activate ZnO in visible light for solar water splitting, although the PEC activities are still not high.

As a physical doping method, ion implantation has been reported to be an effective approach, because it is able to make the metal ions inject into the bulk of semiconductor and modify the electronic structures of semiconductors. Furthermore, this method can control the concentrations of different dopants by tuning the implantation doses. Takeuchi et al. [18] implanted Cr ions into TiO_2 thin film for NO decomposition under visible light irradiation. The results showed that the extent of red shift increased with increasing amounts of Cr ions implanted and Cr ions didn't work as recombination centers. TiO_2 implanted with V, Mn, Ni and Fe ions also showed optical absorption efficiently red shifted to visible light region and exhibited excellent photocatalytic activity under visible light irradiation [19–22]. Some successes have been achieved by ion implantation to activate wide band gap semiconductors like TiO_2 in visible light region, however, there is still rare report on ions implanted ZnO nanorod arrays (NRs) for PEC water splitting under visible light [23].

In this study, ZnO NRs were grown on the fluorine-doped tin oxide (FTO) via a hydrothermal method. V ions were then successfully injected into ZnO NRs by the ion implantation method at room temperature to form impurity levels to expand its optical absorption to visible light region. As a result, the V ions implanted ZnO NRs showed considerable PEC performances under visible light illumination (λ > 420 nm). The effects of implanted V ions on the morphological, optical and PEC properties of ZnO NRs were investigated in detail.

Experimental section

Samples preparation

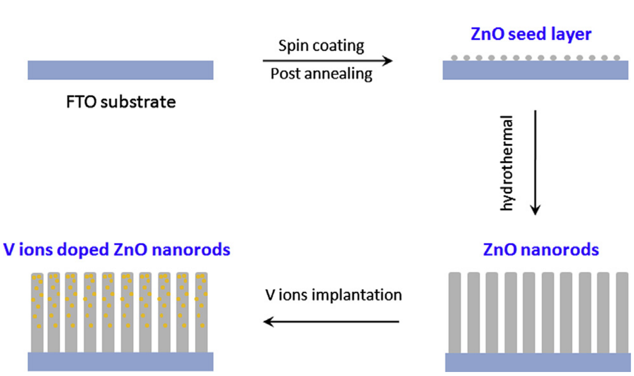
ZnO NRs were grown on F-doped SnO_2 (FTO) substrates via a hydrothermal method as described by Greene et al. [24] with minor modification. A solution of zinc acetate in methanol (0.1 M) was spin-coated on FTO (TEC-15 15 Ω/sp) substrate at 2500 rpm for 20 s, and then annealed in air at 350 °C for 30 min. The seeded substrates were suspended horizontally in a mixed aqueous solution of zinc nitrate (0.05 M) and hexamethylenetetramine (0.05 M) in an 100 mL Teflon-lined autoclave, heated to 90 °C for 24 h. The obtained white ZnO films were then annealed at 500 °C for 2 h with a ramping rate of 2 °C/min. V ions were implanted into the ZnO NRs by metal vapor vacuum arc (MEVVA) ion source implanter [10,11]. This synthesis procedure was carried out at room temperature with accelerator voltage of 50 kV, and the nominal fluences were 2.5×10^{14}, 5×10^{14}, 1×10^{15}, 2.5×10^{15} and 5×10^{15} ions/cm^2, respectively. The obtained V ions doped ZnO NRs with different implantation fluences (2.5×10^{14}, 5×10^{14}, 1×10^{15}, 2.5×10^{15} and 5×10^{15}) were named as V/ZnO-1, V/ZnO-2, V/ZnO-3, V/ZnO-4 and V/ZnO-5, respectively.

Characterization

X-ray diffraction (XRD) patterns were obtained on a PANalytical X'pert MPD Pro X-ray diffractometer using Ni-filtered Cu Kα irradiation (Wavelength 1.5406 Å). The absorption spectra of the samples were determined with a Hitachi U-4100 UV–vis-near-IR spectrophotometer. The samples morphology was observed by a JEOL JSM-7800FE scanning electron microscope and FEI Tecnai G2 F30 S-Twin transmission electron microscope. The chemical composition was obtained by X-ray photoelectron spectroscopy (XPS) (Axis UltraDLD, Kratos) with mono Aluminum Kα radiation. The charge calibration was done by correcting C1s line of adventitious carbon setting to 284.8 eV to compensate the charge effect. Raman scattering study was performed on a Jobin Yvon LabRAM HR spectrometer using an argon ion laser with 514.5 nm irradiation at 20 mW. Photoluminescence (PL) spectra (excited at 340 nm) were tested on a PTI QM-4 fluorescence spectrophotometer.

Photoelectrochemical measurement

Photoelectrochemical (PEC) measurements were carried out in a convenient three-electrodes cell. Pure ZnO and V ions doped ZnO NRs films as working electrodes were mounted onto a special designed electrode holder. The surface areas exposed to electrolyte were fixed at 0.785 cm^2. An Ag/AgCl electrode was used as the reference electrode and a large area platinum plate was used as the counter electrode. An aqueous solution of Na_2SO_4 (0.5 M) was prepared as the electrolyte. An electrochemical workstation (CHI760D) and a 300 W Xe lamp solar simulator (100 mW/cm^2) with adjustable power settings through an AM 1.5 G filter (Oriel) were used for amperometric photocurrent-potential (I–V) and photocurrent-time (I–t) measurements, and a 420 nm cut-off filter was used to prevent



Scheme 1 – Fabrication process for V ions doped ZnO NRs.