



Activation of a highly oriented columnar structure of ZnFe_2O_4 for photoelectrochemical water splitting: Orchestrated effects of two-step quenching and Sn^{4+} diffusion

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ABSTRACT

In present work, we synthesized ZnFe_2O_4 nanorods on a fluorine-doped tin oxide substrate using spray coating method followed by two-step high-temperature quenching (HTQ). X-ray photoelectron spectroscopy (XPS) results indicate that Sn^{4+} is diffused from the FTO substrate after the second quenching, which could help in minimizing the recombination of photogenerated carriers. Photoelectrochemical measurements of the ZnFe_2O_4 nanorod photoelectrodes quenched at 780 °C, 800 °C, and 820 °C indicate that among the studied samples (ZFO1, ZFO2 and ZFO3), the highest photocurrent density was observed for nanotextured ZFO3 photoelectrodes ($130 \mu\text{A cm}^{-2}$ at 1.23 V vs RHE). The photoelectrochemical performances of the ZnFe_2O_4 nanorods after the second quenching were compared with those of the firstly quenched ZnFe_2O_4 nanorod samples; water-oxidation photocurrent density of the former (ZFO3) was increased by 6.9 times compared with that of the first quenching (PZFO). Intensity modulated photocurrent spectroscopy (IMPS) and photoluminescence (PL) results confirm the faster charge extraction was achieved for the ZFO3 photoelectrode. Thus, the overall photocurrent density during the second quenching process results from the effectively improved crystallinity, the reduced strain and suppressed charge-carrier recombination's on both the surface as well as in the bulk of the ZnFe_2O_4 nanorods. In terms of solar water splitting, these research findings provide an effective route for the synthesis of other nanostructures.

1. Introduction

To meet the world's increasing energy demand; a significant objective of researchers over the last decade is the use of semiconductor photoelectrodes for efficient generation of hydrogen from photoelectrochemical (PEC) water splitting [1–4]. Metal oxide semiconductors including tungsten trioxide (WO_3) [5], iron(III) oxide ($\alpha\text{-Fe}_2\text{O}_3$) [6], zinc oxide (ZnO) [7], and bismuth vanadate (BiVO_4) [8] are promising photoanode materials for PEC cells mainly because of their suitable band positions for solar water splitting [9]; however, the several limitations of these materials include insufficient optical bandgaps and poor electric properties, and these seriously impede the attainment of a

high solar-to-hydrogen (STH) conversion efficiency [10–15]. Thus, the search for new photoelectrodes with a high energy-conversion efficiency, narrow bandgap, and proper band potential has become necessary. To fulfil these requirements, the development of numerous elemental doping and compound-semiconductor photocatalysts with modified surface and structural properties has been achieved. But still, the PEC performance is not satisfactory. A high number of the desired properties of $\alpha\text{-Fe}_2\text{O}_3$, however, are shared with iron (Fe)-based ternary oxides that are classified as ferrites (MFe_2O_4), where M represents the divalent ions such as those zinc (Zn^{2+}), calcium (Ca^{2+}), and magnesium (Mg^{2+}) [16–18]. Among these spinel ferrites, spinel zinc ferrite (ZnFe_2O_4) has been widely studied as a promising photoelectrode

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candidate due to its narrow bandgap of approximately 2.0 eV [19], a low surface-recombination rate, and a low onset potential, thereby allowing the water-splitting reaction to proceed at a lower external bias [20]. Additionally, ZnFe_2O_4 is rarely used as a photoelectrode on heat-sensitive transparent conductive-oxide substrates due to its high crystallization temperature. Many reports have shown that it is difficult to fabricate a photoelectrode on a heat-sensitive transparent conductive-oxide substrate, because ferrite crystallization requires an extremely high temperature [19,21]. Consequently, the charge-transport properties are the major challenges that need to be overcome before this material can be used for practical applications. Doping can mitigate some of the deficiencies such as low electrical mobility, short hole diffusion length, however, the measurement of dopant concentrations and interpretation of the role of dopants on material properties remains challenging [22]. To enhance the efficiency of pure ZnFe_2O_4 photoanodes, the metal-ion incorporation or the doping of ZnFe_2O_4 with different metals such as titanium (Ti) [23], manganese (Mn) [24], and magnesium (Mg) [25] has recently been successfully achieved, and have shown improved electrical and optical properties.

However, only modest improvements in photocurrent have been realized by iteratively varying the dopant type, quantity, and/or synthesis method [26]. Recently, photoelectrochemical performance of $\alpha\text{-Fe}_2\text{O}_3$ has been improved by diffusion of tin (Sn) atoms from the fluorine doped Tin Oxide (FTO) glass substrate and incorporated into $\alpha\text{-Fe}_2\text{O}_3$ thin film by high temperature (800 °C) sintering [27]. Thus, post-annealing of $\alpha\text{-Fe}_2\text{O}_3$ thin film based photoelectrode with self-doped Sn atom can be an alternative approach to solution-based doping for improvement of photoelectrochemical performance [28]. It is also worthwhile to point out that the construction of nanotextured photoanodes is another fruitful approach to improve the light absorption and carrier collection, due to the larger surface area [29,30]. Recently, to adjust the electronic structure and overcome the poor charge-transport properties, several synthetic strategies for the preparation of high-efficiency ferrite nanostructures have been studied. McDonald et al. reported the formation of a ZnFe_2O_4 shell on a hematite surface using the treatment and modification of the surface of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles by immersing the electrode in a solution containing Zn^{2+} ions, and the photocurrent response was enhanced compared with the pure $\alpha\text{-Fe}_2\text{O}_3$ electrode [31]. Kim et al. synthesized one-dimensional (1-D) ZnFe_2O_4 -nanorod photoanodes using a simple solution method on FTO glass substrates. They used the thermal treatment under a hydrogen or vacuum atmosphere and showed the improved PEC water-oxidation activity that is up to 20 times greater due to the increasing of the donor density and the passivation of the surface states [9]. Presently, attention is being paid to photoanode-array nanostructures to solve the diffusion-length problem of photogenerated holes, and this is due to the formation of nanostructure architectures that improve the charge-collection efficiency by shortening the distance that the charge carriers need to travel for the surface water oxidation [32,33]. Many researchers have used methods such as electrodeposition [34], chemical bath deposition [35], dropping [19] and spraying [23] to prepare nanostructure thin layers. Spray pyrolysis is the most effective process among the synthesis methods because it contributes a high homogeneity, a product purity, and the structure and morphology of the thin films that are subjected to the spray pyrolysis are easily controlled using the starting compound at low processing temperatures, [36,37] therefore, to modify the surface of as-synthesized $\beta\text{-FeOOH}$ using a Zn source, spray methods are significant. Thus, the scope that is available to tackle the problem of an effective charge separation and the transfer and extension of the light absorption in nanocrystalline ZnFe_2O_4 films toward the visible solar-spectrum region is excessive. An attempt has been made for the PEC water splitting regarding the preparation and activation of the $\beta\text{-FeOOH}$ for which a Zn precursor spraying and a two-step annealing process were applied.

In this study, $\beta\text{-FeOOH}$ nanorods were fabricated on an FTO substrate using a hydrothermal method, and then the Zn-precursor solution

was effectively sprayed on the $\beta\text{-FeOOH}$ nanorods using the spray pyrolysis method [38]. The Zn-sprayed $\beta\text{-FeOOH}$ was transformed into the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanorod structure by high-temperature quenching. Additionally, during the high-temperature quenching, the Sn^{4+} was diffused from the FTO substrate to the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$. Further, to remove the ZnO layer from the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ surface, the films were soaked into a 1 M NaOH solution. Lastly, to improve the charge-transfer properties of the ZnFe_2O_4 , the three different second quenching conditions (780, 800, and 820 °C) were employed. The PEC performance for solar water splitting of the ZnFe_2O_4 can be easily tuned and optimized using the second quenching. Thus, the first quenching process is for the transformation from the Zn-sprayed $\beta\text{-FeOOH}$ nanorods to $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ and the activation of the ZnFe_2O_4 . With an increase of the second quenching temperature, however, the Sn^{4+} diffusion and the electron lifetime are also increased. As a result, the photoelectrode prepared at optimal condition (ZFO3) showed the best photocurrent of $130 \mu\text{A cm}^{-2}$ at 1.23 V vs RHE (reversible hydrogen electrode), which is approximately 6.9 times greater compared with the first quenched ZnFe_2O_4 electrode at 1.23 V vs the RHE.

2. Experimental section

2.1. Reagents and chemicals

Iron(III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Aldrich, Germany), hydrochloric acid (HCl) (Aldrich, U.S.A), Sodium nitrate (NaNO_3) (Aldrich, Japan), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2$) (Aldrich, Germany) were acquired for the experiments. All of the reagents were of analytical grade and were used as received without further purification.

2.2. Preparation of the ZnFe_2O_4 photoanodes

The FTO glass substrates were ultrasonically cleaned using acetone, ethanol, and deionized water, respectively. The cleaned FTO glass substrates were kept in a 20 mL vial containing 10 mL of an aqueous solution of 0.15 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 M NaNO_3 with a pH of 1.5 that was adjusted using HCl. Further, solution-containing vials were kept in an oven at 100 °C for 6 h. Synthesized yellowish $\beta\text{-FeOOH}$ films on the FTO substrates were cleaned in deionized water several times to remove the surface particles and dried under N_2 gas purging. Then, 5 mL of a 50 mM $\text{Zn}(\text{NO}_3)_2$ solution in ethanol was coated onto the $\beta\text{-FeOOH}$ films using spray pyrolysis. The nozzle-to-substrate distance 15 cm was kept constant and the solution flow rate was maintained at 5 mL/min. Then, the films were sintered at 800 °C for 13 min to convert the Zn-sprayed $\beta\text{-FeOOH}$ nanorods into $\text{ZnFe}_2\text{O}_4/\text{ZnO}$. Moreover, during the first quenching, the small amount of Sn^{4+} was diffused from the FTO substrate into ZnFe_2O_4 , and to remove the excess ZnO layer, the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ substrate was soaked into a 1 M NaOH solution for 12 h with stirring. After the removal of the ZnO layer, further ZnFe_2O_4 photoanodes were quenched at different temperatures (780, 800, and 820 °C for 13 min) as shown in Scheme 1. This second quenching treatment was used to improve the Sn^{4+} diffusion, thereby suppressing the charge-carrier recombination to allow for the extraction of the latent solar water splitting activity of the ZnFe_2O_4 . The ZnFe_2O_4 photoanode that was firstly quenched at 800 °C for 13 min is denoted as “PZFO” in the further discussion of this paper, while the second time quenched ZnFe_2O_4 photoanodes at 780 °C, 800 °C, and 820 °C for 13 min are denoted as “ZFO1,” “ZFO2,” and “ZFO3,” respectively.

2.3. Characterization

For the structural analysis of the grown photoanodes, X-ray diffraction (XRD) measurements were carried out on the 5 A beamline at the Pohang Accelerator Laboratory (PLS-II) in the Republic of Korea. The XRD data were recorded in the conventional θ - 2θ mode with X-rays

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