Effect of sulfur doping on photoelectrochemical performance of hematite

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ABSTRACT

Herein, we report preparation of S-doped α-Fe$_2$O$_3$ with enhanced photoelectrochemical water splitting performance, through simply annealing the hematite photoanodes in a furnace containing small amounts of sulfur powder. Characterization results (from XRD, SEM, EDX, UV–vis, FTIR, and XPS) showed successful incorporation of sulfur species into the hematite lattice. Considering obtained results, cationic substitution of sulfur (S^{4+}) in hematite lattice was more probable than its anionic substitution (S^{2-}). In addition, partial reduction of Fe^{3+} species to Fe^{2+} followed by increase in oxygen vacancy sites, led to higher charge carrier mobility through polaron hopping mechanism. Higher mobility reduces recombination rate of photo-generated charge carriers in hematite, and as a result, photocurrent produced by the hematite photoanode showed 4 times increase after simple sulfur doping process. The synthesized S-doped hematite is highly stable and shows no performance decline under continuous illumination. Moreover, electrochemical impedance studies indicated that charge transfer at the surface of the photoanode has facilitated after sulfur doping.

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1. Introduction

Photoelectrochemical (PEC) solar energy conversion, or simply artificial photosynthesis, has been well studied since its first introduction by Fujishima and Honda [1]. Since then, manipulating and adapting various semiconductors to simultaneously capture, convert, and store solar energy became the main research topic in photoelectrochemistry. Hematite (α-Fe$_2$O$_3$) potentially can satisfy most of the initial conditions to be employed as the photoanode for artificial photosynthesis. It has 2.1 eV band gap, with proper energy level of valence band, and sccan be synthesized with low cost, it is also highly stable in aqueous environments [2–4]. These characteristics rarely can be found in other semiconductors, but like the other materials, hematite has intrinsic limitations that made scientists to look for solutions to overcome them. High recombination rate, short hole diffusion length, low absorptivity, and poor oxygen evolution reaction kinetics are examples of such disadvantages [5,6]. In this regard, different strategies can be applied, which can be summarized as elemental doping [7,8], employing oxygen evolution reaction (OER) catalysis [9,10], and nano-scale morphological modification through various synthesis processes [11–13].

Few years ago, Xia et al. proposed that substitutional doping of sulfur on oxygen cites can decrease the band gap of hematite [14]. From their calculations, the direct band gap of 1.45 eV can be achieved when the concentration of S in α-Fe$_2$O$_{3-x}$S$_x$ reaches the value of 5.6%. Complete sulfurization of hematite results to another semiconductor, pyrite with 0.95 eV band gap which is a promising material for photovoltaic applications [15]. The calculations of Xia et al. were based on an assumption that the doping mechanism is substitution of oxygen sites by sulfur (substitutional doping of S^{2-}), however there is another possibility that the other oxidation states of sulfur might be doped into the hematite lattice and replace iron sites (substitutional doping of S^{4+} and S^{6+}). Generally, reports concerning non-metal doping of hematite for PEC applications, either theoretical or experimental, are scarce. Nguyen et al. studied the role of oxygen vacancy cites and nitrogen doping on photoelectrochemical activity of hematite, by density functional theory calculations. They claimed that formation of oxygen vacancy cites and nitrogen doping can result in 0.2 to 0.3 V reduction in the water oxidation over potential [16]. While there is no experimental report for successful S-doping on hematite for PEC water splitting, there are some reports concerning waste water treatment and organic degradation [17,18]. On the contrary,

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S-doping of several metal oxides like TiO_2, WO_3, ZnO, and $BiVO_4$ have been studied thoroughly in recent years [19–22]. In most of those reports, the enhanced photoelectrochemical activity of sulfur-doped samples is attributed to the band gap reduction. In TiO_2 for example, Umebayashi et al. prepared S-doped TiO_2 by oxidation heating of TiS_2, and proposed that substitution of O^{2-} by S^{2-} was the main reason for the band gap variation [23]. On the other hand, Bayati et al. reported cationic doping of sulfur on TiO_2 by micro arc oxidation method, which substitution of Ti^{4+} by S^{4+} and S^{6+} was observed. The resulted S-doped TiO_2 had 2.29 eV band gap which is significantly lower than un-doped samples (~ 3.0–3.2 eV) [24]. Fairly similar results were reported by other groups [25,26]. In addition, calculations presented by Raybaud et al. showed that the formation of partially delocalized electronic levels above valence band is responsible for the band gap narrowing of S-doped TiO_2. The findings of their results suggest that cationic S-doping systems (S^{4+} or $S6^+$) are more stable than anionic doping (S^{2-}), and based on their thermodynamic studies, achieving anionic S-doping in real experiments are very unlikely to happen [27].

Since there is no experimental report regarding S-doped α-Fe_2O_3 for PEC water splitting, we performed a study to investigate the effect of sulfur doping on photoelectrochemical activity of hydrothermally synthesized hematite. The presented doping method was very simple, included annealing the hematite photoanodes in a furnace containing small amounts of sulfur powder. The results were far from expectations, and shed light to a simple, but omitted way of improving photoelectrochemical activity of hematite.

2. Experimental

2.1. Materials and synthesis

The commercially available materials were used without further purification. Ferric chloride ($FeCl_3.6H_2O$, 98%), sodium nitrate ($NaNO_3$, 98%) and acetone (($CH_3)_2CO$, 99.5%) were obtained from Daejung Chemicals & Metals. Sulfur (S, 99%), ethanol (C_2H_5OH, 99.9%), potassium hydroxide (KOH, 99%), sodium hydroxide (NaOH, 99%) and hydrochloric acid (HCl, 37%) were from Merck. Fluorine-doped tin oxide coated glass (FTO, TEC15) were purchased from Dyesol. The deionized water was from regional water purification companies and used as purchased.

FTO slides (1×2.5 cm) were washed by acetone, ethanol and deionized water respectively and dried at room temperature. 25 mL of 0.1 M ferric chloride and 1 M sodium nitrate with pH adjusted to 1.2 by hydrochloric acid and sodium hydroxide, was poured in a Schott bottle. Top of the conductive sides and the entire non-conductive sides of FTO substrates were covered by Parafilm to prevent deposition on those parts. FTO slides were vertically placed in the bottle, then the reactor was heated at 100 °C for 4 hours in an oven. The as-prepared β-FeOOH layers were transparent yellowish which were washed with deionized water before being dried at ambient temperature. In order to obtain the reddish brown layer of hematite (α-Fe_2O_3), the electrodes were annealed at 700 °C for 60 minutes with heating rate of 6 °C/min. Sulfur doped electrodes were prepared by further annealing of the pristine hematite electrodes in presence of sulfur powder in various amounts (0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1 g sulfur powder per 10 cm^2 of deposited hematite film). Electrodes and sulfur powder were placed in the regular furnace, and heated at 450 °C for 30 minutes with heating rate of 6 °C/min, and left to cool down to room temperature. Further details are available at the supporting information (Fig. S1). Fairly similar procedure was reported by Li et al. for synthesis of sulfur doped V_6O_{13} [28].

2.2. Characterization

X-ray diffraction (XRD) was carried out using EQUINOX-3000, Inel. The morphologies of the samples were observed by a field emission scanning electron microscope (FE-SEM). Atomic percentages of elements at the surface of the electrodes were obtained by energy dispersive X-ray spectroscopy (EDX). Both FE-SEM and EDX measurements were performed by Mira3-XM, TESCAN. UV–vis spectra were recorded by JASCO V-670 UV–vis spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded with JASCO FT/IR-6300 FTIR spectrophotometer. The X-ray photoelectron spectroscopy (XPS) spectra was obtained using BESTEC XPS instrument, operated with Al Kα X-ray source, and the whole spectra was calibrated by C 1 s reference peak (284.6 eV).

2.3. Photoelectrochemical and electrochemical measurements

Solar illumination was simulated by a 300W white LED lamp, while light intensity was fixed at 1000 W.m^2 by TES 1333 solar power meter. All photoelectrochemical and electrochemical experiments were conducted in 1 M KOH solution, and oxygen was eliminated from the solution by nitrogen purging. A potentiostat-galvanostat (Autolab PGSTAT302N) was used for PEC and electrochemical measurements. A three-electrode cell, consisting prepared electrodes as working electrode, platinum as counter electrode, and Ag/AgCl/KCl as reference electrode was used. The reference electrode was filled with 3 M KCl solution. The voltammograms were recorded at a scan rate of 10 mV sec^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were performed under applied AC voltage with 10 mV amplitude and frequency ranged from 0.1 Hz to 10 KHz. Mott-Schottky plots were obtained using FRA potential scan procedure in the NOVA 1.9 software, while the potential ranged from 0.2 to −0.7 V vs. Ag/AgCl/KCl.

3. Results and discussions

3.1. Characterizations

The figures presented on this paper are based on pristine hematite and S-doped hematite electrode with 0.25 gr sulfur loading which had the highest photoelectrochemical performance. Detailed results are presented in the supporting information.

The XRD spectra of pristine and S-doped hematite are presented in Fig. 1. The Bragg's diffraction peaks of the photoanodes can be identified as α-Fe_2O_3 and SnO_2 with reference patterns JCPDS 24-0072 and JCPDS 46-1088 respectively. No new phases can be identified after sulfur doping, which have seen before in doped hematite photoanodes [29–31]. On the other hand, small systematic shift of the diffraction peaks to higher angles indicate that sulfur doping caused to tensile stress induction in hematite [32,33]. Since ionic radius of S^{4+} (37 picometer) and S^{6+} (12 picometer) are lower than Fe^{3+} (49 picometer) and O^{2-} (140 picometer) [34], sulfur doping can introduce macro stresses in hematite structure. It is worth mentioning that such interpretation is delicate and needs careful considerations, since misalignment of samples in XRD instrument can produce specimen displacement error, which can be a cause of systematic peak position shift. In this regard, replication on XRD data was conducted and similar shifts were recorded.

EDX analysis shows that sulfur content at the surface of photoanodes linearly increases with amount of sulfur loaded at the sulfur doping step (Fig. S2). Moreover, SEM images of pristine and S-doped hematite (Fig. 2) show that sulfur doping had not significant effect on particle size, however the S-doped hematite has a little higher surface roughness and more defects than pristine