



Tantalum and aluminum co-doped iron oxide as a robust photocatalyst for water oxidation

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ABSTRACT

Efficient and stable photocatalysts for water oxidation are highly sought after in the field of photoelectrochemical (PEC) water splitting. Herein, a new type of tantalum and aluminum co-doped iron oxide (Ta/Al-Fe₂O₃) material was fabricated by a simple drop coating method. XPS analysis suggests that Ta and Al were successfully co-doped into Fe₂O₃ and Ta can greatly influence the chemical environment of Al and O on the surface of catalyst. The resultant optimum (0.25%)Ta/(10%)Al-Fe₂O₃ film presented excellent enhanced PEC activity and photostability. A 15 times higher photocurrent density as well as two times higher incident-photon-to-current efficiency (IPCE, 430 nm) can be clearly observed relative to (10%)Al-Fe₂O₃ at 0.35 V vs. Ag/AgCl. The dramatic enhanced PEC and IPCE performance are attributed to mixed effects induced by tantalum doping, such as positive shift of flat band potential (ca. 50 mV), a reduction in anodic overpotential for water oxidation and greatly reduced charge transfer resistance, which eventually facilitate more efficient separation and easier transfer of photogenerated electron-hole pairs. The highly improved visible light activity and film stability indicate that tantalum and aluminum co-doped iron oxide will be a promising semiconductor for water oxidation.

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1. Introduction

Photoelectrochemical (PEC) water splitting into hydrogen and oxygen has been regarded as one of the most promising strategy for collecting and storing the harvested solar energy on a global scale [1–4]. However, it still remains a great challenge to develop an efficient semiconductor electrode under visible light irradiation which accounts up to ca. 43% sunlight [5]. Basically, the most promising photoelectrodes should have the properties of appropriate band edges for targeted reactions, good cycling stability, environmental friendliness and low cost. In addition, a simple and inexpensive electrode preparation method is also pivotal for potential application.

Among various semiconductors, Fe₂O₃ has emerged as a strong candidate in the photoassisted water oxidation reaction since it has favorable band gap (2.0–2.2 eV), the necessary valence band position for oxygen evolution, stability against corrosion, nontoxicity and ample abundance [6]. The theoretical maximum solar-to-hydrogen efficiency is as high as 15% when Fe₂O₃ is used as a photoanode [7]. However, these favorable characteristics are balanced against its low conductivity, a miserably short excited state lifetime, a short hole diffusion length, high recombination

of photogenerated electron-hole pairs and the need of a large applied potential for producing a photocurrent [6,8,9].

Considerable efforts have been focused on improving the PEC activities of Fe₂O₃ by incorporating noble metals into Fe₂O₃. For example, Pt, Pd, Au or Ag [10–13] doped Fe₂O₃ all exhibited significantly enhancement of PEC performance due to suppressed recombination and promoted transportation of photogenerated charge carriers by the incorporation of noble metals. Incorporating metal cations such as Si, Ti, Al, Mo, Cr, Nb [14–22] has also been proven to be effective methods for increasing carrier concentrations and hence conductivity. Meanwhile, surface modifications with water oxidation catalysts such as IrO₂, Co-phosphate or Co nanoparticles (NPs) [23–28] would improve reaction kinetics and reduce overpotentials. However, previous researches concern much on single substrate modification, little attention has been paid to photoelectrodes with simultaneously two substances modification, which were found to exhibit potentially more excellent PEC performance [29]. For example, Jang et al. screened Ag for hematite with a scanning electrochemical microscopy and found that 50% Ag–50% Fe with addition of 2% Sn achieved an optimum photocurrent response as that compared to Ag–Fe binary oxides [13]. Sartoretti et al. reported that Fe₂O₃ doped with Al/Ti or Zn/Ti increased the hole diffusion length and consequently exhibited more attractive PEC activity than Fe₂O₃ thin films [30]. Despite wide attempt to overcome the intrinsic limitations of Fe₂O₃, the efficiency of Fe₂O₃ semiconductor electrodes for PEC water splitting still falls far from satisfactory and fabricating ternary iron

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oxides offers immense potential to achieve a robust photocatalyst for PEC water oxidation.

In this study, a new type of ternary iron oxides was developed as a robust water oxidation catalyst by introducing tantalum and aluminum cations into Fe_2O_3 to replace iron via simple drop coating method. The structural and PEC performance of Al- Fe_2O_3 and Ta/Al- Fe_2O_3 electrodes were investigated systematically under visible and UV-visible (UV-vis) light irradiation. It was found that a very small amount of Ta (0.25%) co-doping will lead to a huge upgrade on the PEC activity. The resultant optimum ternary Ta/Al- Fe_2O_3 electrode showed a 15 times higher photocurrent density relative to binary Al- Fe_2O_3 electrode. To the best of our knowledge, this is the first report of tantalum and aluminum co-doped into Fe_2O_3 with extremely high PEC performance.

2. Experimental

2.1. Chemicals

Tantalum (V) chloride (TaCl_5) (99.9% purity) was purchased from J&K Scientific Ltd. (Beijing, China). Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) (99.99% purity) and Cobalt (II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) (99.9% purity) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (98.5% purity), Ethanol (99.7% purity), Ethylene glycol (99.5% purity) and Ammonia (25% purity) were available from Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan, China). All chemicals used in this study were analytical grade reagents and were used as received without further purification.

2.2. Synthesis of Ta/Al- Fe_2O_3 , Al- Fe_2O_3 and Fe_2O_3 films

A simple drop coating method was used to prepare the photocatalyst films. The procedures are as follows: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, TaCl_5 were introduced in ethylene glycol at 10 mM to prepare metal precursor solutions. Al- Fe_2O_3 solution was achieved with various Al/Fe molar ratio (0%, 5%, 8%, 10%, 12%, 15%, 20%) by addition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ precursor solution into $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor solution. Ta/Al- Fe_2O_3 solution was obtained by adding TaCl_5 precursor solution into Al- Fe_2O_3 solution (molar ratio of Al/Fe was 10%) with various molar ratio of Ta/Fe (0%, 0.1%, 0.25%, 0.5%, 2%). Then the as-prepared solutions (30 μL) were pipetted onto F-doped tin oxide (FTO, Nippon Sheet Glass, Japan) substrate (10 mm \times 10 mm) and dried in a vacuum oven at 80 °C. After repeating this procedure 4 times, the films were heated at 500 °C for 3 h. For Fe_2O_3 films, 10 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was prepared. The other conditions for drop coating and heat treatment were identical to those of Al- Fe_2O_3 and Ta/Al- Fe_2O_3 films.

2.3. Preparation of Co_3O_4 NPs as oxygen evolution catalysts

Co_3O_4 NPs were synthesized based on a literature process [28]. Briefly, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.5 g) was dissolved in ethanol (25 mL) and ammonia (25%, 2.5 mL) was added under vigorous stirring for 10 min, forming a homogeneous viscous slurry. The suspension was transferred into an autoclave (50 mL), sealed, maintained at 150 °C for 3 h and then cooled to room temperature. Ta/Al- Fe_2O_3 , Al- Fe_2O_3 films were immersed in the resulting freshly prepared Co_3O_4 NPs solution (2 mL) for 3 h, washed with distilled water and then dried in air to fabricate Ta/Al- $\text{Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$ and Al- $\text{Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$ films.

2.4. PEC experiments

PEC experiments were conducted in a three-electrode configuration equipped with an Ag/AgCl reference electrode and a

platinum counter electrode at room temperature. A potentiostat (CH Instruments, model 660D) was used to perform electrochemical measurements. The electrodes were irradiated with light from a Xe lamp fitted with a cut-off filter to achieve visible light and the resulting incident intensity was ca. 100 mW cm^{-2} . All films were back-illuminated through the FTO glass. Photocurrents were measured in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 aqueous solution (pH 9.3) or in 0.2 M NaOH aqueous solution (pH 13.3). IPCE measurements were detected with a Xe lamp fitted with different monochromatic filters (400, 430, 450, 475, 500, 550 nm) combined with a power meter (model FZ-A) in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 aqueous solution. Mott–Schottky (M–S) plot was obtained using a potentiostat at frequencies of 500, 1000, 3000 Hz and a peak-to-peak amplitude of 5 mV at each potential in 0.2 M NaOH aqueous solution. Nyquist plots were achieved in 0.2 M NaOH aqueous solution with a frequency range of 100–0.01 Hz and a scan rate of 5 mV s^{-1} under dark and bright conditions.

2.5. Surface characterization

The crystal structures of as-prepared samples were characterized by X-ray diffraction (XRD) with a Phillips PANalytical X'PERT diffractometer using a Cu-K α radiation source operated at 40 kV and 40 mA. High resolution transmission electron microscopy (HRTEM) (Philips Tecnai 30 FEI TEM at 300 kV) was used to image the morphology and surface structure of the as-prepared films. Scanning electron microscope (SEM) was performed using an S-4700 (II) (Hitachi) to obtain the thickness of the as-prepared films from side views. X-ray photoelectron spectroscopy (XPS) was acquired using a Kratos Axis Ultra DLD instrument with a monochromatic Al X-ray source to determine the surface atomic compositions and valance states of the samples. The binding energies of Fe 2p, Al 2p, Ta 4f and O 1s were referenced against the C 1s (284.6 eV). The optical property of the films was conducted on an UV-vis spectrophotometer (Shimadzu, UV-vis 2450).

3. Results and discussions

3.1. PEC Activities of Ta/Al- Fe_2O_3 and Al- Fe_2O_3 films

Various synthetic conditions were tried to develop the highest active photocatalysts based on Fe_2O_3 under visible light irradiation. In the present study, Ta and Al were co-doped into Fe_2O_3 . The PEC activities of the as-prepared films were characterized by linear sweep voltammetry (LSV) method in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 aqueous solution (pH 9.3) under visible light ($\lambda > 420 \text{ nm}$) irradiation. Na_2SO_4 served as the electrolyte and Na_2SO_3 served as a sacrificial electron donor to consume the photoinduced holes at the semi-conductor/electrolyte interface. Since sulfite oxidation was much easier than water oxidation, higher photocurrents could be obtained in 0.1 M Na_2SO_4 with 0.1 M Na_2SO_3 aqueous solution for the same photocatalysts. Thus, the minor difference in PEC activities among various Al/Fe and Ta/Fe molar ratio photocatalysts based on Fe_2O_3 could be easily found. The photocurrent densities as a function of applied potential (I - V) for different Al- Fe_2O_3 films were first tested. As illustrated in Fig. 1a, the photocurrent densities of Fe_2O_3 are greatly enhanced after aluminum doping in the full tested potential range, and the optimum performance is observed at 10% Al/Fe molar ratio. The results are in accordance with the improved activity achieved by electrodeposited aluminum doped hematite [19]. As for Ta/Al- Fe_2O_3 , different Ta/Fe molar ratio and constant Al/Fe value (10%) were tested. The I - V relationships are depicted in Fig. 1b, and the highest performance can be achieved on (0.25%)Ta/(10%)Al- Fe_2O_3 film. SEM images of (0.25%)Ta/(10%)Al- Fe_2O_3 and (10%)Al- Fe_2O_3 films (see Figure S1

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