

Comparative study of photo-excited charge carrier dynamics of atomic layer deposited and solution-derived hematite films: Dependence of charge carrier kinetics on surface orientations

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ABSTRACT

Charge carrier kinetics of hematite films prepared via atomic layer deposition and solution-derived methods were investigated using heterodyne transient grating technique in aqueous solution, depending on bias voltage, to reveal the effects of surface orientation differences on the charge carrier dynamics. We found that the electron/hole recombination in atomic layer deposited hematite was slower than that in solution-derived hematite, indicating the generated charge carriers in atomic layer deposited hematite can survive longer than that in solution-derived hematite, which is usually beneficial for water oxidation. On the other hand, the trapping dynamics of the long-lived holes to the surface state for water photo-oxidation in the solution-derived hematite was observed at faster time region than that in atomic layer deposited hematite, implying that the diffusion of the holes in atomic layer deposited hematite was slower than that in solution-derived hematite due to the different barrier height and width of the space charge layer which strongly depends on the surface orientations. It means that the low charge carrier mobility rather than the retardation of the charge recombination in the atomic layer deposited hematite is a dominant factor in its low photoelectrochemical performance.

1. Introduction

Since the industrial revolution, human life has been rapidly developed with aid of great technological advances. However, simultaneously, humanity has suffered from very serious environmental pollution, caused by burning of fossil fuels. Another problem is that the amount of fossil fuels in our earth are limited, which means it will be totally exhausted eventually, followed by a decline of human civilization. Thus, finding alternative energy sources has been regarded as one of the most urgent issues in modern times. There have been many attempts for the development of the alternative sources of energy [1–16] and one of them is to produce hydrogen and oxygen gases using solar energy as renewable energy sources by splitting water that exists on Earth almost infinitely [9,2–16]. It has been realized since 1972 when Fujishima and Honda succeeded in demonstrating the water splitting process for the first time [11]. In this study, they built a photoelectrochemical (PEC) cell in which TiO₂ was employed as a photoanode. By irradiation of UV light, TiO₂ absorbed it and generated photo-

excited charge carriers, electrons and holes. Some of them were trapped at the surface and, by using the trapped holes, water oxidation process took place on the TiO₂ surface, generating O₂ gas.

Since then, several kinds of semiconductor materials have been demonstrated as the photoanodes for water oxidation [12–16], and hematite, the mineral form of iron (III) oxide (α -Fe₂O₃), has been regarded as one of the best materials for the purpose because it is inexpensive, earth-abundant and photostable [16–19]. In order to prepare hematite films, many preparation methods have been reported so far [20–28], with one of most-used methods is the atomic layer deposition (ALD) method [21,28]. In the ALD method, it is possible to grow materials uniformly with high precision. Thus, it has been considered one of the best methods with great potential for fabricating very thin and high quality films and employed for making hematite films in the early stage due to its advantages [29].

Another facile technique for fabricating films is to make them derived from solution consisting of precursors, which is called a solution-derived (SD) method [21]. There are reports that SD hematite appears

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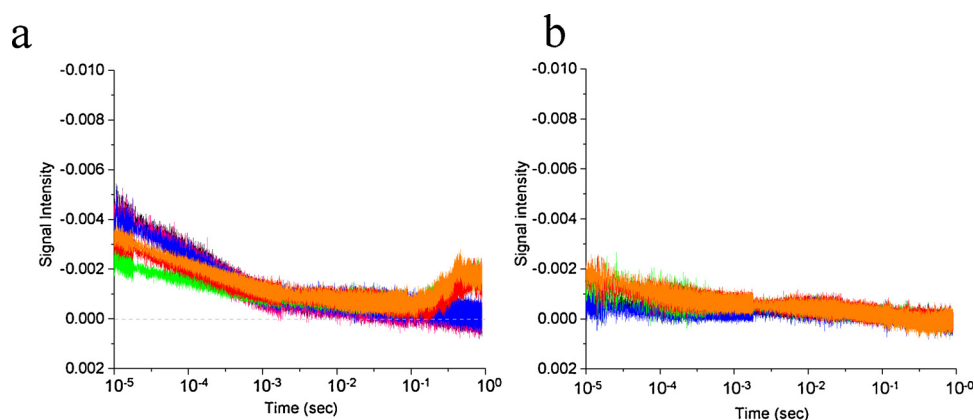


Fig. 1. HD-TG responses of hematite films prepared via a) ALD and b) SD methods, depending on the applied bias voltage (vs. Ag/AgCl), colored with black (0.0 V), pink (0.5 V), blue (0.8 V), green (1.1 V), red (1.4 V), orange (1.7 V) ranged from 10^{-5} to 1 s. The HD-TG response of SD hematite from ref. 34 was reproduced by permission of the Elsevier Owner Societies 2018.

to favour growth of (110) planes [21], giving rise to a morphological change and an increase in surface area [30], to which the higher PEC performance of SD hematite could be attributed.

It has been understood that the charge carrier dynamics in semiconductor materials strongly depends on the surface orientations. For example, it has been reported that the relaxation time of the photo-excited charge carriers on TiO₂ (110) and (011) -2×1 is different [31] and the oxidation and reduction reaction sites are separated into each (001) and (101) face in anatase TiO₂ due to the charge transport direction [32].

In addition, it has been also well known that the surface orientations of the semiconductor materials strongly influence the barrier height and width of the space charge layer, which directly affect charge separation efficiency and diffusion of the charge carriers [33]. Because the surface orientations of ALD and SD hematite are different, it can be expected that not only just the morphology but also charge carrier dynamics, such as the charge mobility from the bulk to the surface, influence the PEC performance.

Therefore, in this study, we investigated photo-excited charge carrier kinetics of the ALD hematite film and compared it to that of SD one, which was previously investigated [34], and demonstrated that the charge carrier dynamics of hematite strongly depends on the fabrication methods. In addition, we clearly revealed the correlation between the PEC performance and the charge carrier dynamics.

2. Experimental

In this study, we prepared the hematite films using the ALD method. In order to prepare them, an atomic layer deposition apparatus (Cambridge Nanotech, Savannah 100) was used. Iron tert-butoxide (heated to 125 °C) and water (25 °C) were used as the precursors for hematite and were pulsed alternately into the deposition chamber (heated to 180 °C) with a $10 \text{ cm}^3 \text{ min}^{-1}$ flow of N₂ as carrier gas. 500 cycles were used to produce the hematite films 20–30 nm in thickness, grown onto FTO. Following the deposition, the samples were annealed at 500 °C for 15 min in air to assure all samples were completely converted into hematite.

To deposit NiFeOx, Iron(III) 2-ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals) and nickel(II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals) were mixed in hexane to give a concentration of 15% w/w metal complex solution. The solution was further diluted 10 times with hexane and approximately $10 \mu\text{L cm}^{-2}$ of this solution was directly drop-casted onto the hematite electrodes. After drying in air for 5 min, the sample was treated with ozone for 3 h to remove excess organic precursors. The thickness of amorphous NiFeOx is less than 1 nm.²¹ The structural characterizations of the films used in this study were already conducted in the former studies. [21,35],

For the heterodyne-transient grating (HD-TG) measurement, in

which the refractive index change, induced by photo-chemical or photo-physical processes, is monitored and is sensitive to the dipole change at the solid/liquid interface, the third harmonic output of a Nd:YAG (YAG) laser (355 nm, $\sim 1 \text{ mJ/pulse}$, 10 Hz, pulsewidth:5 ns) and a semiconductor laser (638 nm) were used as pump and probe lasers, respectively. The grating spacing used in the present measurements was 70 μm . The sample was pumped by the irradiation of UV light and the response was measured via the diffraction of the probe light. The signal was detected by a photodiode (Thorlabs, DET110, rise time:14 ns) and amplified by a voltage amplifier (Femto, DHPVA). To eliminate the scattered pump light entering the detector, a filter for cutting 355 nm light was also placed in front of the entrance of the detector. It was monitored and recorded by an oscilloscope (Agilent, DSO8104 A, 4GSa/s). In order to observe the response in the time scale between 0.1 s and 1 s, the repetition rate of the pump laser was changed from 10 Hz to 1 Hz using a digital functional generator (DF1906).

In order to measure the HD-TG response under the bias voltage condition, we built a PEC cell consisting of three electrodes: the hematite film as a working electrode, a Pt counter electrode and a reference electrode (Ag/AgCl/3 M NaCl, SSC). They were placed into a quartz cell (3/Q/40, Starna scientific) filled with electrolyte solution (NaOH, pH = 12.5, 0.01 M LiClO₄). A potentiostat (HA-B, Hokuto denko) was employed to apply a bias voltage.

3. Results and discussion

TG responses of ALD hematite were measured in an aqueous solution, depending on the applied bias voltage, and is shown in Fig. 1a. In addition, for comparison, that of SD hematite, which was already reported in the previous study [34], was also presented in Fig. 1b. As can be seen in the figures, the responses can be classified into two components appearing in fast and slow time regions. In the fast time region, 10^{-5} - 10^{-3} seconds, the first decay component was observed in both cases, which was already assigned to the electron-hole recombination dynamics arising from the surface trapped holes.³⁶ On the other hand, each response shows totally different features in the second component, appearing around 10^{-1} and 10^{-2} seconds in bare ALD and SD hematite, respectively. In bare ALD hematite, it shows a rising response starting from 10^{-1} second and decayed while SD hematite shows only a decay response.

The time constants of these responses were extracted by maximum entropy method (MEM), which is one of the statistical analyses to yield a continuous distribution of lifetimes of discrete exponential responses by maximizing the data entropy using the noise amplitude as a prior information, enabling to decide the number of exponential functions to appropriately fit the observed responses [37], and the obtained time constants are listed in Table 1.

As can be seen in the table, the time constants of the decay of the first component in bare ALD hematite ($\tau = \sim 160 \mu\text{s}$) were much larger

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