Photocatalytic oxygen evolution on α-Fe$_2$O$_3$ films using Fe^{3+} ion as a sacrificial oxidizing agent

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Photocatalytic oxygen evolution on α-Fe$_2$O$_3$ films was studied using the Fe^{3+} ion as a sacrificial oxidizing agent. The reaction conditions affecting the oxygen evolution rate, *i.e.* anion, Fe^{3+} concentration, pH, Fe^{3+}/Fe^{2+} equilibrium concentration and dependence of irradiation wavelength, were investigated. The reaction rate increased with increase of both the Fe^{3+} ion concentration and the solution pH. Oxygen evolution ceased at an Fe^{3+} : Fe^{2+} ion concentration ratio of 3 : 7–4 : 6. The reaction rate decreased rapidly for longer-wavelength irradiation (above around 400 nm), which is considerably shorter than the α-Fe$_2$O$_3$ bandgap of *ca.* 600 nm (2.1 eV).

1. Introduction

Oxygen evolution from water using photocatalysts with UV irradiation has been intensively studied.[1-6] However, reports of research based on visible light irradiation are limited.[7-9] The α-Fe$_2$O$_3$ photoelectrode has received considerable attention as a solar energy conversion material because of its excellent properties, such as a small bandgap, high resistivity toward corrosion and low cost. This material has especially been used as a photoanode for the photoassisted electrolysis of water.[10] The energy band position of α-Fe$_2$O$_3$ is located favorably for the oxidation reaction of water to oxygen; the flatband potential has been reported to be -0.1 V *vs.* SCE at pH 6.3.[11] Although α-Fe$_2$O$_3$ has been extensively investigated as a photoelectrode, it has rarely been applied as a photocatalyst for oxygen evolution. Iron oxide in a hydrous form has been studied previously.[7,8] Apart from oxygen evolution, the α-Fe$_2$O$_3$ photocatalyst has been used for the oxidation of CN$^-$, SO$_3$$^{2-}$,[12,13] or halide ions.[14] It was also reported that the hydrous ferric oxide had better results than a TiO$_2$-based catalyst in the photogeneration of NH$_3$.[15]

In this paper we studied photocatalytic oxygen evolution on α-Fe$_2$O$_3$ films using the Fe^{3+} ion as a sacrificial oxidizing agent. The reaction conditions which affect the oxygen evolution rate, such as anion effect, Fe^{3+} concentration, pH effect, Fe^{3+}/Fe^{2+} equilibrium concentration and dependence of irradiation wavelength, were investigated. The properties of the Fe^{3+} ion as a sacrificial agent for oxygen evolution have been studied previously in other semiconducting powder photocatalyst systems.[6,9] The use of the Fe^{3+} ion has the advantage over, *e.g.* the S$_2$O$_8$$^{2-}$ ion[8] that the reaction is thermodynamically far more uphill (favorable for energy conversion from light to chemical energy) because the redox potential of Fe^{3+} is more negative than S$_2$O$_8$$^{2-}$. It is also advantageous over the Ag$^+$ ion[7] because Fe^{3+}/Fe^{2+} is a reversible redox couple which exists in the solution phase whereas the Ag$^+$ ion can be reduced to Ag only by being deposited on the photocatalyst surface. The α-Fe$_2$O$_3$ films were fabricated by RF magnetron sputtering. α-Fe$_2$O$_3$ can be formed by various methods such as sputtering, chemical vapor deposition (CVD), sintering or flame oxidation of iron metal. Here we applied sputtering, which is a relatively controllable method in which the deposition parameters (film thickness, substrate temperature, RF power, deposition atmosphere and pressure, *etc.*) can be changed for characterization and optimized in future studies.

2. Experimental

The α-Fe$_2$O$_3$ film was deposited on a glass substrate by RF magnetron sputtering from an Fe$_2$O$_3$ target (Furuuchi Chemical) in an argon atmosphere. The applied input power was 100–150 W, which provided a deposition rate of 0.3–0.7 Å s^{-1}. Photocatalytic oxygen evolution was performed at room temperature using a closed gas-circulating system. The details of the system have been described previously.[16] The α-Fe$_2$O$_3$ film sample and the aqueous solution containing the Fe^{3+} ion were introduced into a quartz reaction cell. After the reaction cell was deaerated and substituted with 60 kPa Ar, the cell was irradiated with a 250 W high-pressure Hg lamp (USHIO, ML-251A/A). The gas evolved on irradiation was analyzed using gas chromatography (Ar carrier, Yanaco-G2800). Fe^{3+} and Fe^{2+} ion concentrations were determined by measuring UV–vis absorption spectra after complexation with thiocyanic acid for the Fe^{3+} ion and with 2,2′-dipyridyl for the Fe^{2+} ion.

3. Results and discussion

It was found from the XRD spectrum that the sample consisted of α-Fe$_2$O$_3$ (Fig. 1). The α-Fe$_2$O$_3$ film started to absorb light from *ca.* 600 nm corresponding to a bandgap of 2.1 eV (Fig. 2), which is the typical bandgap value of α-Fe$_2$O$_3$ reported in the literature.[17] Fig. 3 shows the amount of oxygen which was evolved by successive irradiation. The reaction cell was evacuated and refilled with 60 kPa Ar repeatedly after each experimental cycle of irradiation, and subsequent gas analysis was fulfilled. In most experiments the oxygen evolution rate decreased gradually over the first few hours and then approached a constant value. Oxygen evolution was not observed in the absence of Fe^{3+} ion in solutions, and the reaction was apparently found to be catalytic from the fact that oxygen evolved in amounts far more than the stoichiometric amount from the α-Fe$_2$O$_3$ samples, with a film thickness of 1 μm, typically engaged in the present study. Similar results were even obtained using samples with a film thickness of 300 Å.
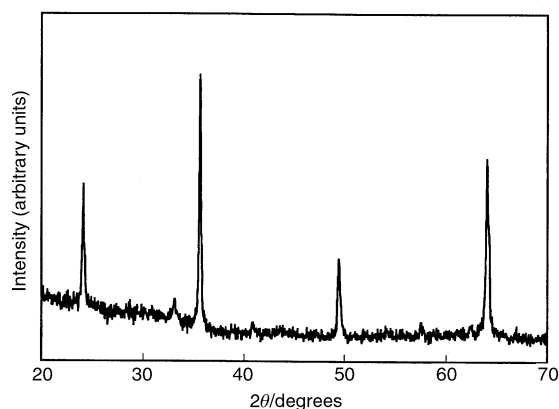
Fig. 1 XRD pattern for the film deposited by RF magnetron sputtering.

The oxygen evolution rate was greater in 1 M $Fe[(NO)_3]_3$ (pH 0.6) than in 1 M $FeCl_3$ (pH 1.0). However, this is considered to result from an event such as decomposition of the NO_3^- ion. It was confirmed that oxygen was evolved on irradiating the α-Fe_2O_3 film in HNO_3, or even from HNO_3 alone, thus leading to excess oxygen evolution regardless of the photocatalytic reaction. In 0.5 M $Fe_2(SO_4)_3$ (pH 0.6) oxygen did not evolve owing to its low pH value, which reduced the photocatalytic reaction activity, as will be described below. Hereafter, we focussed on an investigation of the photocatalytic oxygen evolution reaction using $FeCl_3$ solutions.

On increasing the Fe^{3+} ion concentration, the oxygen evolution rate increased. For instance, at pH 1.8 oxygen evolution was not observed in 0.001 M $FeCl_3$, while oxygen evolved at an initial rate of 0.9 μmol h^{-1} cm^{-2} in 0.1 M $FeCl_3$ (we used the term 'initial rate' for the amount evolved during the first hour of irradiation). An increase in the Fe^{3+} ion concentration led to a decrease in the solution pH. Therefore, if the Fe^{3+} ion concentration was simply changed (*i.e.* without
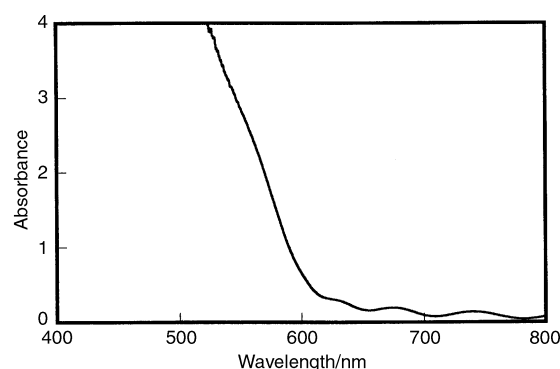

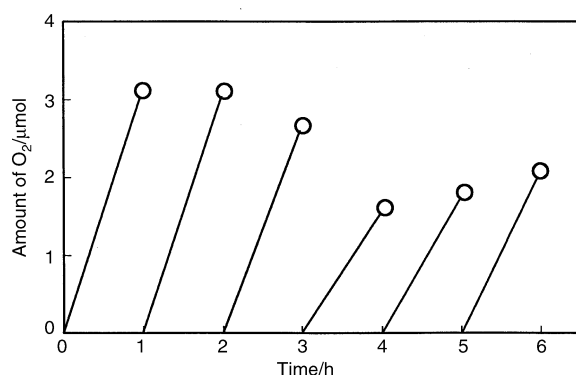**Fig. 2** Absorption spectrum of the α-Fe_2O_3 film.

Fig. 3 Oxygen evolved with successive irradiation in 1 M $FeCl_3$.

adding other electrolytes in order to keep the pH constant), the effect of pH on the reaction rate had to be taken into account at the same time. The initial oxygen evolution rate increased up to 4 μmol h^{-1} cm^{-2} in 1 M $FeCl_3$. The pH of 1 M $FeCl_3$ (pH 1.0) could not be increased so as to compare the results because precipitation of iron hydroxide occurred.

The oxygen evolution rate decreased as the solution pH decreased. As seen in Table 1, the initial oxygen evolution rate decreased with decrease in pH in 0.1 M $FeCl_3$. When the Fe^{3+} ion concentration was adjusted to 0.0064 M $FeCl_3$, the amount of evolved oxygen became larger at pH 0.82 than at pH 1.7 on prolonged irradiation. This was caused by the photodissolution reaction of the α-Fe_2O_3 film, which involved oxygen evolution. It was observed that the α-Fe_2O_3 film peeled off from the glass substrate, broke into small pieces and dissolved in the solution. The α-Fe_2O_3 photoanodic dissolution reaction, which is accompanied by oxygen evolution, is written as follows at pH 1:[10,18]

$$Fe_2O_3 + 6h^+ \rightarrow 2Fe^{3+}(aq) + \tfrac{3}{2}O_2$$
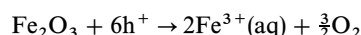
It was suggested that stability toward photoanodic dissolution could be achieved if the Fermi level of the redox couple in solution were more negative than the decomposition potential, E_D.[19,20] According to this criterion, α-Fe_2O_3 should be stable in the pH range for which the O_2/H_2O level is more negative than E_D of the above reaction (typically >pH 0) in the present system. The dissolution reaction rate will be affected not only by pH but also by Fe^{3+} ion concentration, as is found from the above equation. It is considered that the dissolution was effectively suppressed in 1 M $FeCl_3$, while it proceeded readily in 0.0064 M $FeCl_3$ under low pH conditions. The observed pH dependence on the photocatalytic oxygen evolution rate could be explained by the fact that the flatband potential of α-Fe_2O_3 is shifted according to the Nernstian formula[11] with the oxidation potential of water to oxygen, while the standard redox potential of Fe^{3+}/Fe^{2+} moves in the positive direction with increasing solution pH.[21] Other factors, such as ion adsorption onto the α-Fe_2O_3 surface, may need to be considered simultaneously.

We examined how much oxygen would evolve from a given initial Fe^{3+} ion concentration before the photocatalytic oxygen evolution reaction ceased. With an initial concentration of 0.01 M $FeCl_3$, oxygen continued to evolve until the Fe^{3+} ion was consumed to reach a concentration of *ca.* 0.003 M (Fig. 4). For this calculation, it was assumed that one oxygen molecule evolved with the concomitant reduction of four Fe^{3+} ions to Fe^{2+}. Accordingly, the concentration ratio between Fe^{3+} and Fe^{2+} ions in the equilibrium state is estimated to be 3 : 7. Further, the absorption spectra were measured for the Fe^{3+} and Fe^{2+} ions, respectively, by withdrawing a portion of the solution after the reaction, and the concentration ratio was evaluated as 4 : 6. The experimental error was within 25% through all the experiments between the values calculated from the amount of oxygen evolution and from the absorption spectra. The equilibrium concentration ratio was approximately the same (3 : 7–4 : 6) for an

Table 1 Oxygen evolution rate at various pH values. The initial oxygen evolution rate is shown in 0.1 M $FeCl_3$ while the total amount of oxygen which evolved during prolonged irradiation is presented in 0.0064 M $FeCl_3$

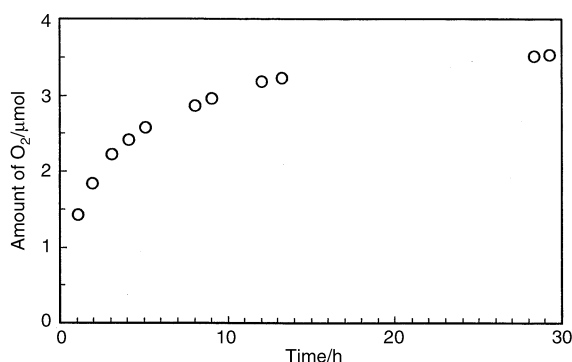| Fe^{3+} concentration 0.1 M		Fe^{3+} concentration 0.0064 M	
pH	Amount of $O_2/$ μmol h^{-1} cm^{-2}	pH	Amount of $O_2/$ μmol
0.76	0.35	0.82	1.8
1.8	0.94	1.7	0.74
2.2	1.1	2.6	1.5

Fig. 4 Cumulative amount of oxygen evolved with successive irradiation. The solution used was 0.01 M FeCl$_3$ with amount of 2 ml.

initial concentration of 0.001 M FeCl$_3$. The forward and backward reactions of $Fe^{3+} + e^- \rightarrow Fe^{2+}$ are considered to become equilibrated at this Fe^{3+} : Fe^{2+} concentration ratio. We also performed an experiment in which the concentration ratio was initially regulated at $[Fe^{3+}]/[Fe^{2+}] = 1$ ($[Fe^{3+}]$, $[Fe^{2+}] = 0.005$ M) before the irradiation was started. Here, oxygen evolution was hardly observed, demonstrating that the Fe^{3+} ion concentration in the initial solution was already lower than that in the equilibrium state. This result supports the above idea concerning the equilibrium state, although it gave a different equilibrium concentration ratio (5 : 5), which could arise as a result of different experimental procedures. It was reported that oxygen evolution occurred above an Fe^{3+}/Fe^{2+} molar ratio of $ca.$ 0.2 in the WO$_3$ photocatalyst system,[22] while oxygen continued to evolve until all of the Fe^{3+} ion was thoroughly reduced to become Fe^{2+} ion in the TiO$_2$ system.[6] In the latter case, the equilibrium concentration ratio was considerably reduced because the Fe^{3+} ion adsorbed preferentially over the Fe^{2+} ion onto the TiO$_2$ surface. Noticeable adsorption of Fe^{3+} ion onto the α-Fe$_2$O$_3$ surface was not observed in the present study, which was confirmed from measurement of the Fe^{3+} ion concentration in solution. One important factor for facilitating photocatalytic reactions would be to design the photocatalytic system so that the sacrificial reacting species can be favorably adsorbed onto the surface.

The dependence of oxygen evolution on the irradiation wavelength was examined by measuring the reaction rate using low-frequency pass filters. As seen in Table 2, the reaction rate decreased rapidly for irradiation of longer wavelength. Oxygen was not detectable when the 460 nm filter was used, although the α-Fe$_2$O$_3$ film was shown to absorb light from $ca.$ 600 nm. In the case of an Fe$_2$O$_3$ colloidal photocatalyst it was reported that the quantum efficiency decreased from a maximum at around 400 nm with increasing irradiation wavelength.[7] Moreover, in a study of water photo-oxidation on an α-Fe$_2$O$_3$ electrode,[23] the absorption

coefficient calculated from the photocurrent was smaller than that obtained from optical measurements in the longer-wavelength range. Hence our result accords with these studies. One possible reason for the observed wavelength dependence might be the fact that there exist two types of electronic transition in α-Fe$_2$O$_3$.[24,25] The first is the transition which takes place from the Fe^{3+}(3d) band and the second is that from the O^{2-}(2p) band. The hole mobility which is generated in the Fe^{3+}(3d) band will be lower compared to that in the O^{2-}(2p) band because of the narrowness of the d band. The energy required for the former transition (the onset is 2.1 eV for the bandgap excitation) is typically smaller than for the latter transition (an energy larger than $ca.$ 3.0–3.5 eV is necessary[26,27]). Consequently, the above wavelength dependence might be because the hole mobility is lower (with the result that the number of holes which can reach the surface is smaller) in the former transition (generated by irradiation of a longer wavelength) than in the latter one (generated with a shorter wavelength). In addition to the hole mobility, the charge transfer site is also different between the two transitions,[25] which could be another explanation for the experimental results. A similar case was made regarding water photo-oxidation with an α-Fe$_2$O$_3$ electrode: the hole in the O^{2-}(2p) band could react to evolve oxygen while that in the Fe^{3+}(3d) band could not.[23] In addition to these, it has been reported that the holes (electrons) created by shorter-wavelength light than the bandgap can reach the surface without being thermalized in the valence (conduction) band, leading to a higher reaction rate for shorter wavelength light.[7,28] All these factors confirm our results, but further detailed investigations including the surface states,[17,29] which affect the recombination process, must be done in order to clarify the mechanism.

In conclusion, photocatalytic oxygen evolution on α-Fe$_2$O$_3$ films has been studied using Fe^{3+} ion as a sacrificial oxidizing agent. The reaction conditions affecting the oxygen evolution rate, such as anion effect, Fe^{3+} concentration, pH effect, Fe^{3+}/Fe^{2+} equilibrium concentration and dependence of irradiation wavelength, were investigated. The reaction rate increased with increase of both the Fe^{3+} ion concentration and the solution pH. The optimum solution condition for the reaction was 1 M FeCl$_3$; the NO_3^- and SO_4^{2-} anions had the disadvantage of being decomposed on irradiation or of lowering the solution pH, and the highest concentration of FeCl$_3$ gave the fastest reaction rate even at the expense of the lowest pH, with suppression of the α-Fe$_2$O$_3$ dissolution effectively. Oxygen ceased to evolve at an Fe^{3+} : Fe^{2+} concentration ratio of 3 : 7–4 : 6. The reaction rate decreased rapidly for longer wavelength irradiation above around 400 nm, although the absorption started from $ca.$ 600 nm, for which a further detailed study is needed. The reaction efficiency would be expected to be improved on optimizing the α-Fe$_2$O$_3$ photocatalyst, by changing the sputtering conditions or by depositing RuO$_2$ on the α-Fe$_2$O$_3$ film.

Acknowledgements

Table 2 Oxygen evolution rate observed using optical cut-off filters[a]

	No filter	390 nm filter	430 nm filter	460 nm filter
Amount of O$_2$/ μmol h^{-1}	3.7	0.35	0.0045	—[b]
Light intensity/ W	2.7	0.90	0.32	0.13
Quantum efficiency		0.3	0.1	0.003

[a] The filter wavelength denotes the cut-off wavelength at 50% transmittance. The light intensity is also presented for each irradiation, measured by a laser power meter. Each quantum efficiency value (from the left-hand side) shows the value at wavelength below 390 nm, between 390 and 430 nm, and between 430 and 460 nm, respectively. [b] Below the detection limit.

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