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Photoelectrochemistry of Hematite

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Abstract

It was possible to prepare a hematite film by electrochemical deposition of iron oxide in aqueous solution and its heat treatment at 500°C or higher temperature in air. The deposition process of iron oxide film from current and potential pulse methods was mentioned in relation to the equilibrium potential for iron oxide. The hematite in aqueous solution showed a clear photoanodic current due to visible light irradiation. The photo-oxidation response of hematite electrode to organic and inorganic materials in aqueous solution was summarized through the examples of citric acid, Pb²⁺ and aniline.

Keywords: iron oxide, electrochemical deposition, hematite, photoelectrochemistry, visible light

1. Introduction

Hematite (α -Fe₂O₃), one of iron oxides, has merits of abundance, harmlessness and stability. Hematite is expected to be utilized as a photo-functional material for the purpose of conversion of visible light energy to chemical and electric energy because it is an n-type semiconductor with band gap energy of about 2.0 eV. There are several reports concerning photoelectroc-hemical characteristics [1–7], photo-oxidation of water [8–15] and photocatalytic water purification [16–21] by using hematite. It is known that oxygen evolution due to photo-oxidation of water could occur on the hematite irradiated with visible light. This may be an interesting and important process from the viewpoint of artificial photosynthesis. Hematite is also one of the candidates for photocatalyst acting under visible light irradiation. Titanium dioxide with band gap energy of about 3.0 eV shows strong photocatalytic performance for environmental purification such as air purification, anti-soiling, self-cleaning, deodorizing, water purification and anti-bacterial [22–23], but it has disadvantage for utilization of visible light energy. In order to use hematite for photocatalysis and photosynthesis effectively, it is necessary to make clear its

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photoresponse to chemical species. Knowledge about hematite electrode/electrolytic solution interface is important to understand a reactivity of photo-generated hole in the valence band of hematite to chemical species during irradiation. For the use of hematite as a photo-functional material, preparation of hematite film may be useful from the aspect of its repetitive performance. We have prepared the hematite film by electrochemical deposition of iron oxide and its heat treatment, and studied photo-oxidation of organic and inorganic materials on the hematite photoelectrode. Investigation of photo-oxidation of organic materials on hematite may lead to a new development of organic materials synthesis based on visible light energy conversion.

In this chapter, I would like to describe photoelectrochemistry of hematite in terms of electrochemical preparation of iron oxide film, photoelectrochemical characterization of hematite and photo-oxidation reaction of chemical species on hematite mainly based on the results we have obtained [24–29].

2. Electrochemical preparation of iron oxide film

On photocatalysis and photo-conversion by using hematite, preparation of hematite film is useful from the point of view of repetitive performance. Iron oxide film is prepared by spray pyrolysis, electrochemical deposition, sputtering method and so on. Electrochemical method may provide easy and reproducible preparation of iron oxide film. Here, based on the results we have obtained, the current and potential pulse deposition process of iron oxide film is mentioned as follows.

2.1. Current pulse deposition of iron oxide film

An iron oxide film (geometric surface area of 1.0 cm^2) was prepared on a titanium substrate by current pulse deposition with repetition of cathodic pulse (current (I_c); time (t_c): 1 s) and anodic pulse (current (I_a); time (t_a): 1 s) as shown in **Figure 1**. The surface of titanium substrate was polished with alumina powder, immersed in aqueous HCl solution, washed with pure water and cleaned ultrasonically before electrolysis. The working electrode of titanium substrate and



Figure 1. Current pulse deposition of iron oxide film with repetition of cathodic pulse (current: $I_{c'}$ time: $t_c = 1$ s) and anodic pulse (current: $I_{a'}$ time: $t_a = 1$ s).

the counter electrode of iron plate were connected to a potentio-galvanostat with a function generator. The aqueous solution of 10 mM FeCl₂–0.15 M NaCl (pH = 4.4) under oxygen gas bubbling was used for the electrochemical deposition of iron oxide film. The temperature of this solution was kept constant at 25°C by circulation of thermo-stated water [29, 26].

Figure 2 shows the potential of titanium working electrode during the electrolysis by repetition of cathodic pulse ($I_c = -7 \text{ mA}$, $t_c = 1 \text{ s}$) and anodic pulse ($I_a = +1 \text{ mA}$, $t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under O₂ bubbling for 100 s. The potential changed periodically with the cathodic and anodic current pulses. The potential depending on anodic current pulse approached to the value of -0.68 V vs. Ag/AgCl gradually. In the case of galvanostatic deposition with the current of -7 mA for 50 s in the same solution as above, the potential of working electrode became almost constant value of -1.60 V vs. Ag/AgCl.

Figure 3 shows the XRD of the film by current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) for 100 s, the upper representing the pattern of the film after heat treatment at the temperature of 600°C for 1 h in air and the lower pattern corresponding to the as-deposited film before heat treatment. The diffraction peaks of Fe₃O₄ (magnetite) and FeO (wustite) and the peaks of α -Fe₂O₃ appeared on the film before and after heat treatment, respectively. On the as-deposited film by galvanostatic reduction (current: -7 mA) for 50 s in the presence of O₂, the diffraction peaks of Fe_{(OH)₂, FeO and Fe were confirmed, but the peak of Fe₃O₄ was not observed. From a consideration of the XRD result, the reaction for the formation of iron oxide film by current pulse deposition in the solution with O₂ gas bubbling could be shown as Eqs. (1)–(4). The reaction in the heat treatment of film in air could be represented as Eqs. (5) and (6).}

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
 (1)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
 (2)

$$Fe(OH)_2 \rightarrow FeO + H_2O$$
 (3)

$$3FeO + H_2O \rightarrow Fe_3O_4 + 2H^+ + 2e^-$$
 (4)



Figure 2. Change of electrode potential of working electrode by repetition of cathodic pulse ($I_c = -7 \text{ mA}$, $t_c = 1 \text{ s}$) and anodic pulse ($I_a = +1 \text{ mA}$, $t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under O₂ bubbling for 100 s.



Figure 3. XRD of the iron oxide film deposited on the titanium by current pulse method ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under O₂ bubbling for 100 s (the lower pattern), and heated at 600°C for 1 h in air (the upper pattern). • titanium \bigcirc hematite \square magnetite \diamondsuit wustite \blacksquare titanium dioxide (rutile).

$$2FeO + 1/2O_2 \rightarrow Fe_2O_3 \tag{5}$$

$$2/3Fe_3O_4 + 1/6O_2 \to Fe_2O_3$$
 (6)

Figure 4a shows the SEM image of the film deposited on the titanium by repetition of cathodic pulse ($I_c = -7 \text{ mA}$, $t_c = 1 \text{ s}$) and anodic pulse ($I_a = +1 \text{ mA}$, $t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂– 0.15 M NaCl solution under O₂ bubbling for 100 s, and heated at 600°C for 1 h in air. The film with the thickness of about 1.0 µm had the network morphology. As shown in **Figure 4b**, the film prepared by galvanostatic reduction with the current of -7 mA for 50 s in the same solution as above, and heated in the same condition showed the similar morphology, but less homogeneous deposition compared with the film by the current pulse method.

The current pulse deposition of iron oxide film in the solution under N₂ gas bubbling was compared with that in the solution under O₂ gas bubbling. **Figure 5** shows the potential of titanium working electrode during the electrolysis by repetition of cathodic pulse ($I_c = -7 \text{ mA}$, $t_c = 1 \text{ s}$) and anodic pulse ($I_a = +1 \text{ mA}$, $t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under N₂ bubbling for 100 s. The appearance of iron, wustite and magnetite XRD peaks was confirmed in the as-deposited film due to the repetition of current pulse in this solution as shown in **Figure 6**. The film after heat treatment at 600°C for 1 h in air had the hematite structure. The SEM image of this hematite film is shown in **Figure 7**. The deposition of particles was observed in this film. The hematite film preparation under N₂ bubbling could be represented as the process of current pulse deposition of iron oxide film (Eqs. (7)–(9), (4)) and its thermal oxidation process (Eqs. (10)–(12)).

$$Fe^{2+} + 2e^- \rightarrow Fe$$
 (7)

$$Fe + H_2O \rightarrow FeO + 2H^+ + 2e^-$$
(8)



Figure 4. SEM image of the iron oxide film by current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) for 100 s (a) and galvanostatic reduction (current: -7 mA) for 50 s (b) in aqueous 10 mM FeCl₂-0.15 M NaCl solution under O₂ bubbling, and heated at 600°C for 1 h in air.



Figure 5. Change of electrode potential of working electrode by repetition of cathodic pulse ($I_c = -7 \text{ mA}$, $t_c = 1 \text{ s}$) and anodic pulse ($I_a = +1 \text{ mA}$, $t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under N₂ bubbling for 100 s.



Figure 6. XRD of the iron oxide film deposited on the titanium by current pulse method ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) in aqueous 10 mM FeCl₂–0.15 M NaCl solution under N₂ bubbling for 100 s (the lower pattern), and heated at 600°C for 1 h in air (the upper pattern). \bigcirc hematite \square magnetite \diamondsuit wustite \triangle iron \blacksquare titanium dioxide (rutile).



Figure 7. SEM image of the iron oxide film by current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) for 100 s in aqueous 10 mM FeCl₂-0.15 M NaCl solution under N₂ bubbling, and heated at 600°C for 1 h in air.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$$
 (9)
 $2Fe_3 + 2/2O_{--} + Fe_3O_{--}$ (10)

$$2Fe + 3/2O_2 \rightarrow Fe_2O_3 \tag{10}$$

$$2FeO + 1/2O_2 \rightarrow Fe_2O_3 \tag{11}$$

$$2/3Fe_3O_4 + 1/6O_2 \to Fe_2O_3$$
 (12)

For the electrochemical reactions of (1), (4), (7), (8) and (9), the corresponding equilibrium potentials can be evaluated by using the values of standard chemical potential of -237.178, -157.293, -91.2, -245.211 and -1015.359 KJ/mol [30] as $\mu^{0}(H_{2}O)$, $\mu^{0}(OH^{-})$, $\mu^{0}(Fe^{2+})$, $\mu^{0}(FeO)$ and $\mu^{0}(Fe_{3}O_{4})$, respectively. The equilibrium potentials (versus normal hydrogen electrode, NHE) of (1), (4), (7), (8) and (9) are represented in Eq. (13)–(17).

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$$E_{eq}(O_2/OH^-) = 0.401 - 0.0591 \times \log_{10}a_{OH^-}$$
(13)

$$E_{eq}(\text{Fe}_3\text{O}_4/\text{FeO}) = -0.220 - 0.0591 \times p\text{H}$$
(14)

$$E_{eq}(Fe^{2+}/Fe) = -0.473 + 0.0296 \times \log_{10}a_{Fe^{2+}}$$
(15)

$$E_{eq}(\text{FeO/Fe}) = -0.042 - 0.0591 \times p\text{H}$$
 (16)

$$E_{eq}(Fe_3O_4/Fe) = -0.086 - 0.0591 \times pH$$
(17)

The electrochemical formation of magnetite could be also considered in Eq. (18) and this equilibrium potential is represented as Eq. (19).

$$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^-$$
 (18)

$$E_{eq}(\text{Fe}_3\text{O}_4/\text{Fe}^{2+}) = 1.072 - 0.2364 \times p\text{H} - 0.0886 \times \log_{10}a_{\text{Fe}^{2+}}$$
(19)

The electrochemical reactions concerning hematite are shown in Eqs. (20)–(23).

$$2FeO + H_2O \to Fe_2O_3 + 2H^+ + 2e^-$$
(20)

$$2Fe + 3H_2O \to Fe_2O_3 + 6H^+ + 6e^-$$
(21)

$$2Fe_{3}O_{4} + H_{2}O \rightarrow 3Fe_{2}O_{3} + 2H^{+} + 2e^{-}$$
(22)

$$2Fe^{2+} + 3H_2O \to Fe_2O_3 + 6H^+ + 2e^-$$
(23)

The corresponding equilibrium potential evaluated by using the standard chemical potential of hematite, -743.608 KJ/mol are represented in Eqs. (24)–(27).

$$E_{eq}(\text{Fe}_2\text{O}_3/\text{FeO}) = -0.083 - 0.0591 \times p\text{H}$$
(24)

$$E_{eq}(Fe_2O_3/Fe) = -0.055 - 0.0591 \times pH$$
(25)

$$E_{eq}(\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4) = 0.192 - 0.0591 \times \text{pH}$$
 (26)

$$E_{eq}(\text{Fe}_2\text{O}_3/\text{Fe}^{2+}) = 0.779 - 0.1773 \times p\text{H} - 0.0591 \times \log_{10}a_{\text{Fe}^{2+}}$$
(27)

These standard equilibrium potentials are slightly different from the values in Pourbaix Diagram [31] due to the used standard chemical potential of component. With regard to the equilibrium potential in the case of pH = 4.4 and Fe²⁺ concentration of 10 mM, $E_{eq}(O_2/OH^-)$ is 0.969 (0.747), E_{eq} (Fe₃O₄/FeO) -0.480 (-0.702), E_{eq} (Fe²⁺/Fe) -0.532 (-0.754), E_{eq} (FeO/Fe) -0.302 (-0.524), E_{eq} (Fe₃O₄/Fe) -0.346 (-0.568), E_{eq} (Fe₃O₄/Fe²⁺) 0.209 (-0.013), E_{eq} (Fe₂O₃/FeO) -0.343 (-0.565), E_{eq} (Fe₂O₃/Fe) -0.315 (-0.537), E_{eq} (Fe₂O₃/Fe₃O₄) -0.068 (-0.290) and E_{eq} (Fe₂O₃/Fe²⁺) 0.117 V vs. NHE (-0.105 V vs. Ag/AgCl). The electrode potential approached to the equilibrium potential of Fe₃O₄/FeO system with repetition of anodic current pulse as shown in **Figures 3** and **5**.

2.2. Potential pulse deposition of iron oxide film

Potential pulse method as shown in **Figure 8** is also useful in preparation of iron oxide film [28]. In this case, electrochemical reduction and oxidation occurs with repetition of a periodic change in the working electrode potential between cathodic potential (E_c) with the time of t_c and anodic potential (E_a) with t_a . The working electrode of titanium substrate and the counter electrode of graphite were connected to a potentio-galvanostat with a function generator. The aqueous solution of 10 mM FeCl₂–0.1 M KCl (pH = 4.4) under O₂ or N₂ gas bubbling was used for the electrochemical deposition of iron oxide film.

Figure 9 shows the XRD of the film prepared by potential pulse deposition ($E_c = -1.0$ V vs. Ag/AgCl, $t_a = 1$ s) for 30 min under O₂ bubbling to the solution, the upper representing the pattern of the film after heat treatment at the temperature of 500°C for 1 h in air and the lower that before heat treatment. The magnetite peaks and the wustite peak were observed on the as-deposited film. Because the value of 0.2 V vs. Ag/AgCl of E_a is more positive than the equilibrium potentials of E_{eq} (Fe₂O₃./FeO) of -0.565, E_{eq} (Fe₂O₃/Fe) of -0.537, E_{eq} (Fe₂O₃/Fe₃O₄) of -0.290 and E_{eq} (Fe₂O₃/Fe²⁺) of -0.105 V vs. Ag/AgCl, there is a possibility of anodic formation of hematite. But the hematite peaks did not appear on the as-deposited film. The hematite structure was confirmed after heat treatment. **Figure 10** shows the XRD of the film by potential pulse deposition under N₂ bubbling to the solution before and after heat treatment. The peaks of magnetite and wustite and hematite peaks were observed on the film before and after heat treatment, respectively. **Figure 11** shows the SEM images of the hematite films prepared from the solution with O₂ bubbling and with N₂ bubbling. A different morphology of these hematite films was observed. The deposition state of iron oxide film was



Figure 8. Potential pulse deposition of iron oxide film with repetition of cathodic pulse (potential: E_{cr} time: t_c) and anodic pulse (potential: E_{ar} time: t_a).



Figure 9. XRD of the iron oxide film deposited on the titanium by potential pulse method ($E_c = -1.0$ V, $E_a = 0.2$ V vs. Ag/ AgCl, $t_c = t_a = 1$ s) in aqueous 10 mM FeCl₂–0.1 M KCl solution under O₂ bubbling for 30 min (the lower pattern), and heated at 500°C for 1 h in air (the upper pattern). \bigcirc hematite \Box magnetite \diamondsuit wustite.



Figure 10. XRD of the iron oxide film deposited on the titanium by potential pulse method ($E_c = -1.0$ V, $E_a = 0.2$ V vs. Ag/ AgCl, $t_c = t_a = 1$ s) in aqueous 10 mM FeCl₂–0.1 M KCl solution under N₂ bubbling for 30 min (the lower pattern), and heated at 500°C for 1 h in air (the upper pattern). \bigcirc hematite \square magnetite \diamondsuit wustite.

dependent on current magnitude, potential value and pulse width. A photocurrent response of hematite film was strongly related to the deposition state of iron oxide by current and potential methods.



Figure 11. SEM image of the iron oxide film by potential pulse deposition ($E_c = -1.0 \text{ V}$, $E_a = 0.2 \text{ V}$ vs. Ag/AgCl, $t_c = t_a = 1 \text{ s}$) for 30 min in aqueous 10 mM FeCl₂–0.1 M KCl solution under O₂ bubbling (a) and N₂ bubbling (b), and heated at 500°C for 1 h in air.

3. Photoelectrochemical characterization of hematite

In order to characterize the hematite film in the aspect of a functional material for photocatalytic water purification and artificial photosynthesis, understanding of hematite electrode/electro-lytic solution interface is important. Here, the Mott-Schottky relation and photocurrent response are mentioned as follows.

3.1. Mott-Schottky relation of hematite electrode/electrolytic solution interface

The measurement of capacitance for hematite electrode/electrolytic solution interface is useful in understanding of properties of hematite as an n-type semiconductor. The hematite film connected to a lead wire was used as a hematite working electrode. The capacitance of

hematite electrode/electrolytic solution interface (C) was measured at a different electrode potential (E). At the semiconductor electrode/electrolyte interface, Motto-Schottky relation can be observed as represented by Eq. (28).

$$\frac{1}{C^2} = \frac{2}{eN\varepsilon\varepsilon^0} \left(E - E_{fb} \right) \tag{28}$$

where *e* is the quantity of charge on an electron, *N* the carrier density, ε is the dielectric constant of electrode material, ε^0 is the permittivity of free space and $E_{\rm fb}$ is the flat-band potential corresponding to the potential indicating no band bending of semiconductor electrode.

Figure 12a, **b** shows the plots of $1/C^2$ against *E* in 0.1 M aqueous Na₂SO₄ solution (pH = 5.7) for the hematite electrodes prepared from current pulse deposition (I_c = -7 mA, I_a = +1 mA, t_c = t_a = 1 s) under O₂ bubbling and N₂ bubbling for 100 s, respectively. The capacitance measurement was carried out with the frequency of 1 kHz. The values of flat-band potential (*E*_{fb}) and carrier density (*N*) of these hematite electrodes were -0.57 V vs. Ag/AgCl (-0.35 V vs. NHE) and $1.35 \times 10^{18} \text{ cm}^{-3}$ (a), -0.33 V vs. Ag/AgCl (-0.11 V vs. NHE) and $3.53 \times 10^{18} \text{ cm}^{-3}$ (b) from the intercept of the linear portion extrapolated to the potential axis and its slope by using ε^0 of 120. The Mott-Schottky relation was also confirmed on the hematite electrode



Figure 12. Plots of $1/C^2$ against *E* in 0.1 M aqueous Na₂SO₄ solution (pH = 5.7) for the hematite electrodes prepared from current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) under O₂ bubbling (a) and N₂ bubbling (b) for 100 s.

prepared from potential pulse deposition ($E_c = -1.0$ V vs. Ag/AgCl, $E_a = +0.2$ V vs. Ag/AgCl, $t_c = t_a = 1$ s) under N₂ bubbling for 30 min and heat treatment at 500°C for 1 h in air. In this case, the values of E_{fb} of 0.00 V vs. Ag/AgCl (+0.22 V vs. NHE) and N of 4.52 × 10¹⁸ cm⁻³ were obtained in 1.0 M aqueous Na₂SO₄ solution (pH = 5.9). According to the other researchers, the hematite prepared by thermal oxidation of iron showed E_{fb} of -0.95 V vs. SCE (-0.68 V vs. NHE) and N of about 3×10^{18} cm⁻³ in 1.0 M aqueous NaOH solution [1], and that prepared by a spray-pyrolytic method E_{fb} of -0.74 V vs. SCE (-0.47 V vs. NHE) and N of 2.2 × 10^{20} cm⁻³ in 1.0 M NaOH solution [9]. Supposing a pH dependence of E_{fb} was 59 mV/pH, the value of F_{fb} for above-mentioned hematite in the solution (pH = 5.7) would be -0.19 and 0.02 V vs. NHE. These mean that the values of E_{fb} and N for hematite depend on preparation methods. Because the value of E_{fb} for n-type semiconductor electrode is approximately equal to the potential for the bottom of conduction band, the hematite from current pulse deposition under O₂ bubbling to the solution may have more negative potential of the conduction band.

3.2. Photocurrent response of hematite to visible light irradiation

In the n-type semiconductor electrode/electrolytic solution interface, the Schottky barrier due to the band bending is formed at more positive potential of semiconductor electrode than flatband potential as shown in **Figure 13**. In this case, no currents may flow on the electrode because of the existence of the Schottky barrier in the dark. Under irradiation of the light with higher energy than band gap, the transfer of photo-generated electrons to the bulk and that of holes to the surface of n-type semiconductor could proceed due to the band bending and thus photoanodic current may flow on the electrode.



Figure 13. Interface of n-type semiconductor electrode/electrolytic solution VB: Valence band, CB: Conduction band, e^- : Photo-generated electron, h^+ : Photo-generated hole.

Figure 14a, **b** shows the photocurrent response of the hematite prepared current pulse deposition under O_2 and N_2 bubbling to the solution, respectively. In this case, repetitive on–off irradiation of the visible light (wavelength: 490 nm, light intensity: 3.8 mW/cm²) was supplied to the surface of the hematite electrode at 1.0 V vs. Ag/AgCl in 0.1 M aqueous Na₂SO₄ solution. A clear photoanodic current was observed in both the hematite electrodes, but the hematite from N_2 bubbling showed a higher photocurrent. The hematite prepared from potential pulse deposition under N_2 bubbling also had a higher photocurrent response compared with that prepared under O_2 bubbling.

The photocurrent response of the iron oxide depending on heat treatment temperature (100–600°C) in air is shown in **Figure 15**. In this case, the iron oxide film was prepared from potential pulse deposition ($E_c = -1.0 \text{ V}$, $E_a = +0.2 \text{ V}$, $t_c = t_a = 1 \text{ s}$) under N₂ bubbling for 30 min. The iron oxide treated at different temperatures was irradiated with the visible light (wavelength: 490 nm, light intensity: 3.8 mW/cm²) at the potential of 1.0 V vs. Ag/AgCl in 0.1 M aqueous Na₂SO₄ solution. The XRD of the film with the corresponding heat treatment temperatures is also shown in **Figure 16**. No photocurrent was detected on the



Figure 14. Photocurrent response of the hematite prepared from current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) for 100 s in aqueous 10 mM FeCl₂–0.15 M NaCl solution under O₂ bubbling (a) and N₂ bubbling (b), and heated at 600°C for 1 h in air.



Figure 15. Dependence of photocurrent response of the iron oxide upon heat treatment temperature at 100–600°C in air iron oxide was prepared from potential pulse deposition ($E_c = -1.0 \text{ V}$, $E_a = 0.2 \text{ V}$ vs. Ag/AgCl, $t_c = t_a = 1 \text{ s}$) for 30 min in aqueous 10 mM FeCl₂–0.1 M KCl solution under N₂ bubbling. The as-deposited film (a) was heated at different temperatures of 100°C (b), 200°C (c), 300°C (d), 400°C (e), 500°C (f) and 600°C (g).



Figure 16. XRD of the iron oxide with same heat treatment as that in **Figure 15**. \bigcirc hematite \square magnetite \diamondsuit wustite \bigtriangledown magnemite.

as-deposited film. This suggests that both magnetite and wustite may have no ability as a photoelectrode. The iron oxide film heat treated at 200°C or higher temperature showed a photoanodic current response and a remarked photocurrent was observed on the film heat treated at 500°C. It has been reported that the DTA peak of transition from magnetite to maghemite (γ -Fe₂O₃) and that of transition from magnetite to hematite appeared at about 150 and 480°C, respectively, on the thermal analysis for magnetite particles [32].

From this, both maghemite and hematite have a photocurrent response to visible light, but the response of hematite is much higher. **Figure 17** shows the photocurrent response of the iron oxide film treated at the temperature of 400–500°C. The XRD of the corresponding iron oxide films is shown in **Figure 18**. All the films showed a photoanodic current response. A marked increase in photocurrent was observed on the film treated at 450°C.



Figure 17. Dependence of photocurrent response of the iron oxide upon heat treatment temperature at 400–500°C in air. Iron oxide was prepared from potential pulse deposition ($E_c = -1.0 \text{ V}$, $E_a = 0.2 \text{ V}$ vs. Ag/AgCl, $t_c = t_a = 1 \text{ s}$) for 30 min in aqueous 10 mM FeCl₂–0.1 M KCl solution under N₂ bubbling. The heat treatment temperatures of as-deposited film were 400°C (a), 410°C (b), 420°C (c), 430°C (d), 450°C (e) and 500°C (f).



Figure 18. XRD of the iron oxide treated at different temperatures of 400–500°C in air. The heat treatment temperatures were 400°C (a), 410°C (b), 420°C (c), 430°C (d) and 500°C (e).

The intensity of maghemite XRD peaks on the films decreased with heat treatment temperature from 400 to 420°C and hematite peaks appeared on the film treated at 430°C as shown in **Figure 18**.

Figure 19 shows the relationship between electrode potential and photocurrent on the hematite in 0.1 M aqueous Na₂SO₄ solution during irradiation. This hematite was prepared from the potential pulse deposition under N₂ bubbling and heat treatment at 500°C. In the dark, anodic current did not flow up to the potential of 1.2 V vs. Ag/AgCl. In the irradiation of UV light (wavelength: 365 nm, intensity: 5.5 mW/cm²) to the hematite, the onset potential of photoanodic current was about 0.0 V vs. Ag/AgCl, almost equal to the value of F_{fb} . In the irradiation of visible light (wavelength: 490 nm, intensity: 4.8 mW/cm²), the onset potential was more positive than F_{fb} . This means a necessity of fair band bending for the separation of photogenerated electron-hole pair in the absorption of visible light.

Figure 20 shows the relationship between photocurrent quantum efficiency and wavelength of irradiation light on the hematite at the potential of 1.0 V vs. Ag/AgCl in 0.1 M aqueous Na₂SO₄ solution containing 1 mM hydroxyl acid. The hematite was prepared from the potential pulse deposition under N₂ bubbling and heat treatment at 500°C. The photocurrent quantum efficiency (η_{elec}) represents the ratio of the number of electrons for photocurrent to photon number of incident light. The value of η_{elec} in the presence of hydroxyl acid. The values of η_{elec} at wavelength in the range of 400–500 nm were 22–7, 17–5 and 14–4% in the presence of citric acid, tartaric acid and malic acid, respectively. The lower value of 5–2% in aqueous Na₂SO₄ solution may reflect a slow transfer of photo-generated holes in the valence band of hematite to water molecules. The highest photocurrent response obtained in the presence of citric acid was probably due to a rapid hole transfer to citric acid molecules. According to the reports [33, 34] on zinc oxide and



Figure 19. Relationship between electrode potential and photocurrent on the hematite in 0.1 M aqueous Na₂SO₄ solution under irradiation of visible light and UV light. Hematite was prepared from potential pulse deposition ($E_c = -1.0 \text{ V}$, $E_a = 0.2 \text{ V vs. Ag/AgCl}$, $t_c = t_a = 1 \text{ s}$) for 30 min in aqueous 10 mM FeCl₂–0.1 M KCl solution under N₂ bubbling, and heated at 500°C for 1 h in air. Three relation curves of a, b and c are corresponding to no irradiation, visible light and UV light irradiation, respectively.



Figure 20. Relationship between photocurrent quantum efficiency and wavelength of irradiation light on the hematite at 1.0 V vs. Ag/AgCl in 0.1 M aqueous Na₂SO₄ solution containing 1 mM hydroxyl acid. Hematite was prepared from potential pulse deposition ($E_c = -1.0$ V, $E_a = 0.2$ V vs. Ag/AgCl, $t_c = t_a = 1$ s) for 30 min in aqueous 10 mM FeCl₂–0.15 M NaCl solution under N₂ bubbling, and heated at 500°C for 1 h in air. Each of citric acid (a), tartaric acid (b) and malic acid (c) was added to aqueous Na₂SO₄ solution (d).

rutile photoelectrodes in aqueous formic acid solution, a distinct increase in photocurrent could be observed because formic acid might act as the hole scavenger of these photoelectrodes. But, a clear increase in photocurrent was not observed on the hematite photoelectrode in formic acid solution.

4. Photoreaction of chemical species on hematite photoelectrode

A photoelectrochemical system consisting of a semiconductor working electrode and a counter electrode may be suitable for performance of water purification and artificial photosynthesis because an effective separation of photo-generated hole and electron pair under irradiation could proceed due to the existence of space charge layer at the semiconductor electrode/ electrolytic solution interface. In the case of using n-type semiconductor, photoanodic oxidation and cathodic reduction occur at a working and a counter electrodes, respectively. Photo-decomposition of water by using titanium dioxide electrode, Honda-Fujishima effect, is well known as a typical photoelectrochemical process. In order to understand photo-oxidation response of hematite to chemical species, we checked oxidation behavior of citric acid, Pb²⁺ ion and aniline on the hematite photoelectrode.

4.1. Photo-oxidation of citric acid on hematite in aqueous solution under visible light irradiation

The HPLC analysis of organic acids in the solution was carried out to reveal the reaction process of citric acid on hematite photoelectrode in aqueous solution [29]. This hematite was



Figure 21. A chromatograms of the citric acid solution before and after irradiation of visible light (wavelength: 490 nm, intensity: 3.8 mW/cm²) to the hematite electrode at 1.0 V vs. Ag/AgCl for 9 hours, b: Relationship among concentration of citric acid, concentration of acetonedicarboxylic acid and irradiation time. Hematite was prepared from current pulse deposition ($I_c = -7$ mA, $I_a = +1$ mA, $t_c = t_a = 1$ s) for 100 s in aqueous 10 mM FeCl₂–0.15 M NaCl solution under O₂ bubbling, and heated at 600°C for 1 h in air.

prepared from the current pulse deposition ($I_c = -7 \text{ mA}$, $I_a = +1 \text{ mA}$, $t_c = t_a = 1 \text{ s}$) under O_2 bubbling for 100 s and heat treatment at 600°C for 1 h in air. **Figure 21a** shows the chromatogram of the aqueous solution of 0.1 M Na₂SO₄ and citric acid (initial concentration: 200 µM) at

the hematite electrode potential of 1.0 V vs. Ag/AgCl. Before irradiation, the only peak due to citric acid was observed at the retention time of 16.5 min. This chromatogram was not changed after immersion of the hematite electrode for 9 h in the dark. After irradiation of the visible light (wavelength: 490 nm, intensity: 3.8 mW/cm²) for 9 h to the surface of hematite electrode, the intensity of the citric acid peak was decreased and a new peak due to acetonedicarboxylic acid appeared at the time of 19.0 min. **Figure 21b** shows the relationship between concentration of citric acid and irradiation time as well as between concentration of acetonedicarboxylic acid and irradiation time. The concentration of citric acid decreased and that of acetonedicarboxylic acid to acetonedicarboxylic acid proceeded on the hematite photoelectrode according to Eq. (29).

$$CH_{2}(COOH)C(OH)(COOH)CH_{2}(COOH) \rightarrow CH_{2}(COOH)COCH_{2}(COOH) +CO_{2} + 2H^{+} + 2e^{-}$$
(29)

Table 1 summarizes the significant values of photocurrent quantum efficiency, quantum efficiency and current efficiency derived from the data of photocurrent measurement and HPLC analysis concerning the photo-oxidation of citric acid on the hematite photoelectrode in aqueous solution under visible light irradiation for 9 h. N_{hv} is the photon number of incident light to the surface of hematite electrode, Q_{elec} is the amount of electric quantity for the photocurrent flowing during irradiation, N_{elec} is the number of electrons from Q_{elec} , η_{elec} is the photocurrent quantum efficiency represented as the term of $(N_{elec}/N_{hv}) \times 100$, ΔC is the change in concentration of citric acid during photo-oxidation from HPLC data, N_{mole} is the number of citric acid molecules oxidized, η_{mole} is the quantum efficiency represented as the term of $(N_{mole}/N_{hv}) \times 100$, and I_{effi} is the current efficiency in the photo-oxidation process of citric acid to acetonedicarboxylic acid. The value of 100.0% was obtained as I_{effi} in the process under visible light irradiation. All the photocurrent was derived from the photo-oxidation of citric acid to acetonedicarboxylic acid. This means that the holes photo-generated by visible light could oxidize only the citric acid molecules.

The HPLC analysis of citric acid under UV light irradiation was carried out to make clear a difference between visible light and UV light affecting the hematite electrode. **Figure 22a** shows the chromatogram of the aqueous solution of 0.1 M Na₂SO₄ and citric acid (initial concentration: 200 μ M) at the hematite electrode potential of 1.0 V vs. Ag/AgCl before and after irradiation of UV light (wavelength: 360 nm, intensity: 4.2 mW/cm²). A distinct decrease in the intensity of citric acid peak and also a distinct increase in that of acetonedicarboxylic acid peak were observed after UV irradiation to the surface of the hematite electrode for 9 h.

$N_{h u}$	Q_{elec} (C)	N _{elec}	η _{elec} (%)	ΔC (µmol)	N _{mole}	η_{mole} (%)	I_{eff} (%)
3.04×10^{20}	0.273	1.71×10^{18}	0.56	1.42	8.65×10^{17}	0.28	100

Table 1. Values in relation to the photoanodic oxidation on the hematite electrode in 0.1 M aqueous Na_2SO_4 solution containing initial concentration of 200 μ M citric acid under irradiation of visible light (wavelength: 490 nm, intensity: 3.8 mW/cm²) for 9 h.



Figure 22. A chromatograms of the citric acid solution before and after irradiation of UV light (wavelength: 360 nm, intensity: 4.2 mW/cm²) to the hematite electrode at 1.0 V vs. Ag/AgCl for 9 hours, b: Relationship among concentration of citric acid, concentration of acetonedicarboxylic acid and irradiation time. Hematite was prepared by the same method as that in **Figure 21**.

Figure 22b shows the relationship between concentration of citric acid and irradiation time as well as between concentration of acetonedicarboxylic acid and irradiation time. The UV light irradiation accelerated the photo-oxidation of citric acid to acetonedicarboxylic acid. **Table 2** summarizes the values concerning photocurrent quantum efficiency, quantum efficiency and current efficiency for the photo-oxidation of citric acid to acetonedicarboxylic acid on the

N _{hv}	Q_{elec} (C)	N _{elec}	η_{elec} (%)	ΔC (µmol)	N _{mole}	η_{mole} (%)	I _{eff} (%)
2.47×10^{20}	1.91	1.19×10^{19}	4.82	6.14	3.70×10^{18}	1.50	62

Table 2. Values in relation to the photoanodic oxidation on the hematite electrode in 0.1 M aqueous Na_2SO_4 solution containing initial concentration of 200 μ M citric acid under irradiation of UV light (wavelength: 360 nm, intensity: 4.2 mW/cm²) for 9 h.

hematite electrode under UV light irradiation for 9 h. The higher value of η_{elec} and η_{mole} means that the UV light could facilitate a transfer of hole of the hematite to the citric acid molecule. This may be ascribed to the photo-generation of a pair of hole and excited electron in the vicinity of the surface of the hematite irradiated with UV light. The I_{effi} value of 62% suggests the occurrence of the photo-oxidation of not only citric acid but also water. This reflects the competitive process of hole transfer to the molecules of chemical species and water in aqueous solution. The I_{effi} value of 100% in the visible light irradiation could be interpreted in terms of the photo-generation of a pair of hole and excited electron at the inside of space charge layer due to a deeper penetration of visible light. In this case, the hole moving from the inside to the surface might prefer citric acid molecule to water molecule probably from the aspect of oxidation rate. The hematite also showed a distinct photo-oxidation response to other hydroxyl acids such as tartaric acid, malic acid and glycolic acid. These results imply possibility of photo-oxidation synthesis of organic materials by using hematite under visible light irradiation.

4.2. Photo-oxidation of Pb^{2+} ion to PbO_2 on hematite in acid solution under visible light irradiation

The photo-oxidation treatment of Pb²⁺ ions in aqueous solution was examined by using hematite for the purpose of elimination of them from the solution [25, 24]. The hematite in this case was prepared from thermal oxidation of iron plate at 600°C for 3 h in air. The cell consisting of the hematite working electrode in 0.1 M HNO₃-10 µM Pb(NO₃)₂ and of the graphite counter electrode in 0.1 M H₂SO₄-10 mM Ce(SO₄)₂ aqueous solution was used as a photocell performing without applied voltage. The flow of photocurrent was observed by irradiation of visible light to the hematite electrode. Figure 23 shows the dependence of photocurrent on irradiation time in this cell and also in the cell with the graphite electrode solution of 0.1 M H₂SO₄-10 mM Fe₂(SO₄)₃ aqueous solution. In this case, the hematite and graphite electrodes acted as a photoanode and a cathode, respectively. It is clear that the presence of Ce⁴⁺ in the cathode solution was effective for the performance of the cell based on the hematite photoanode. Since the standard equilibrium potential of Ce⁴⁺/Ce³⁺ system of 1.44 V vs. NHE is more positive than that of Fe³⁺/Fe²⁺ system of 0.771 V vs. NHE, Ce⁴⁺ may act as a stronger electron acceptor. Figure 24 shows the SEM image of the surface of the hematite electrode before and after irradiation for 6 h in 0.1 M HNO₃-10 µM Pb(NO₃)₂ solution. The photodeposition of many particles was observed on the surface of hematite. The XRD peak due to PbO₂ was confirmed on the hematite after irradiation. This suggests the occurrence of the following photoelectrochemical reactions in Eqs. (30)-(32). The photo-generated hole (h⁺) and electron (e⁻) pair was separated to oxidize Pb²⁺ to PbO₂ by hole at the hematite photoanode and reduce Ce⁴⁺ to Ce³⁺ by electron at the graphite cathode according to Eqs. (30) and (31). The total reaction is represented as Eq. (32). With regard to the standard Gibbs free energy change, ΔG^0 , for reaction (32), the positive value 48.2 kJ/mol could be evaluated by using the standard equilibrium potential of Pb⁴⁺/Pb²⁺, 1.69 V and that of Ce⁴⁺/Ce³⁺, 1.44 V vs. NHE. This means that the reaction (32) is not spontaneous reaction and the light energy causes it to proceed. The hematite prepared from thermal oxidation of iron showed the value of E_{fb} of 0.31 V vs. NHE in the 0.1 M aqueous HNO3 solution. Therefore, the position of valence band edge of hematite



Figure 23. Dependence of photocurrent on irradiation time in the cell consisting of the hematite 0.1 M HNO₃–10 μ M Pb (NO₃)₂ and of the graphite cathode in 0.1 M H₂SO₄–10 mM Ce(SO₄)₂ solution (a) and also in the cell of the photoanode in the same solution and of the cathode in 0.1 M H₂SO₄–10 mM Fe₂(SO₄)₃ solution (b). Hematite was prepared from thermal oxidation of iron at 600°C for 3 h in air.

could be regarded approximately as 2.3 V vs. NHE in the solution (pH = 1) by referring to the band gap energy of 2.0 eV. The occurrence of photo-oxidation of Pb²⁺ to PbO₂ deposition on hematite may be supported by this positive potential of valence band edge. For 0.1 M aqueous HNO₃ solution containing 10 μ M Pb(NO₃)₂, the removal rate of Pb²⁺ ions due to visible light irradiation was checked by atomic absorption analysis. In the case of using Ce⁴⁺ electron acceptor without applied voltage, 8.9% of the initial concentration of Pb²⁺ was removed from the solution after 6 h irradiation. By holding the potential of hematite at 1.50 V vs. Ag/AgCl, a marked increase in the removal rate was confirmed. The values of 27.0, 38.7 and 53.2% were obtained after 2, 4 and 6 h irradiation, respectively.

$$Pb^{2+} + 2H_2O + 2h^+ \rightarrow PbO_2 + 4H^+$$
 (30)

$$2Ce^{4+} + 2e^{-} \rightarrow 2Ce^{3+}$$
 (31)

$$Pb^{2+} + 2H_2O + 2Ce^{4+} \rightarrow PbO_2 + 4H^+ + 2Ce^{3+}$$
 (32)



Figure 24. SEM images of the surface of the hematite electrode before and after visible light irradiation for 6 h in 0.1 M $HNO_3-10 \ \mu M \ Pb(NO_3)_2$ solution. Hematite was prepared from thermal oxidation of iron at 600°C for 3 h in air.

4.3. Photo-polymerization of aniline on hematite and characteristics of polyaniline/hematite electrode under visible light irradiation

The photo-polymerization of aniline was carried out by the photoelectrochemical cell consisting of the separated parts of hematite photoanode in 0.1 M HClO₄–0.1 M aniline and the graphite cathode in 0.1 M H₂SO₄–10 mM Ce(SO₄)₂ aqueous solutions under visible light irradiation [27]. This hematite was prepared from thermal oxidation of iron at 600°C for 3 h in air. These electrolytic solutions were connected by a KCl salt bridge. The deposition of many particles was observed on the surface of the hematite electrode after irradiation. The photoanodic polymerization of aniline due to the photo-generated hole could proceed on the hematite electrode without applied voltage by using Ce⁴⁺ ions as an electron acceptor. Because the potential for the bottom of conduction band is positive as understood from the positive E_{fb} value of hematite, the presence of a strong oxidizing agent as an electron acceptor may be necessary for occurrence of photoelectrochemical reaction on the hematite without application of electric power.

The polyaniline/hematite electrode has a unique property. **Figure 25** (**a**–**c**) shows the Mott-Schottky plots of the hematite electrode, the polyaniline electrode prepared from anodic deposition of polyaniline film on the glassy carbon and the polyaniline/hematite electrode in 0.1 M aqueous HClO₄ solution, respectively, at the frequency of 1 kHz. On the hematite



Figure 25. Mott-Schottky plots of the hematite electrode (a), the polyaniline-glassy carbon electrode (b) and the polyaniline-hematite electrode (c) in 0.1 M aqueous $HClO_4$ solution. Hematite was prepared from thermal oxidation of iron at 600°C for 3 h in air.

electrode in HClO₄ solution, a linear relation due to the n-type semiconductor electrode/ electrolytic solution interface was observed. The value of E_{fb} of the hematite in this solution by extrapolation of the linear line was 0.13 V vs. Ag/AgCl. On the polyaniline electrode in HClO₄ solution, a linear relation due to the p-type semiconductor electrode/ electrolytic solution interface was observed. The state of undoped polyaniline could be regarded as the p-type semiconductor. The value of E_{fb} of undoped polyaniline in this solution was -0.20 V vs. Ag/AgCl. On the polyaniline/hematite electrode in HClO₄ solution, the two linear relations were observed. The linear portion at less positive potential than -0.10 V vs. Ag/AgCl was ascribed to the undoped polyaniline/electrolytic solution interface. Because the doped polyaniline has high electric conductivity to be regarded as metal, the linear portion at more positive potential than 0.12 V vs. Ag/AgCl reflects the hematite/doped polyaniline interface.

The photocurrent on the hematite under visible light irradiation decayed immediately with time at less positive potential than 0.70 V vs. Ag/AgCl in aqueous HClO₄ solution. This means that the band bending of hematite is not enough in this potential range because of slow transfer of photo-generated hole to water molecule. The polyaniline/hematite electrode showed a stable photocurrent response to visible light at less positive potential than 0.70 V vs. Ag/AgCl in aqueous HClO₄ solution. On the polyaniline/hematite electrode, the rapid transfer of photo-generated hole to the polyaniline and simultaneous occurrence of ClO₄⁻ ion doping may proceed. The polyaniline/hematite electrode showed a distinct increase in photocurrent in the presence of glycolic acid. The linear relationship between photocurrent and concentration of glycolic acid (1-10 mM) was recognized under visible light irradiation. On the hematite electrode, the linear dependence of photocurrent on concentration was not observed. This implies a possibility of application of the polyaniline/hematite electrode to an amperometric sensor for glycolic acid. Hematite has the demerit that iron dissolution may proceed in acid solution. The amount of iron dissolution after immersion of hematite in 0.1 M aqueous HClO₄ solution for 1, 2, 3 and 4 h was 4.89, 11.77, 15.18 and 17.55 ppm, respectively, by atomic absorption analysis. The polyaniline/hematite showed the suppression of iron dissolution. The high stability of the polyaniline/hematite in acid solution was supported by the amount of iron dissolution of 0.01, 0.02, 0.03 and 0.04 ppm after immersion in 0.1 M aqueous HClO₄ solution for 1, 2, 3and 4 h, respectively.

5. Conclusion

As a preparation method of hematite film, the process for electrochemical deposition of iron oxide and its heat treatment in air was mentioned in relation to the equilibrium potential of iron oxide in aqueous solution. The current and potential pulse electrolysis may be useful in deposition of homogeneous iron oxide film. The hematite from the heat treatment of iron oxide at 500°C or higher temperature in air showed a clear photocurrent response and brought the photo-oxidation of chemical species such as citric acid, Pb²⁺ ion and aniline under visible light irradiation. On the hematite electrode in aqueous solution containing organic materials under visible light irradiation, photo-oxidation processing of organic materials with suppression of water photo-oxidation may be possible. This will lead to application of photo functionality of hematite to a new method for organic synthesis.

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