

Observation of photoexcitation of Fe-oxide grown on TiO₂(100) by visible light irradiation

Taizo Kawauchi¹ · Naoki Nagatsuka¹ ·
Katsuyuki Fukutani¹

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Abstract Electronic excitation of materials is of fundamental and technological importance and interest in terms of photoinduced phase transition, photovoltaics, and photocatalysis. In the present study, photoexcitation of Fe₂O₃ epitaxially grown on rutile TiO₂(100) was investigated with conversion electron Mössbauer spectroscopy (CEMS) under dominantly visible-light irradiation. ⁵⁷Fe was deposited on the substrate at a substrate temperature of 973 K, and the resulting film was characterized by RHEED and XPS. After deposition of Fe on TiO₂(100), it was found that Fe was oxidized to Fe³⁺, and the structure was analyzed to be the rhombohedral phase of Fe₂O₃. While the CEMS spectrum without light irradiation showed a quadrupole splitting of 0.80 mm/s with an isomer shift of +0.25 mm/s, an additional component with a quadrupole splitting of 0.85 and an isomer shift of +0.67 mm/s was observed under light irradiation. The latter component corresponds to a reduced state of Fe at the octahedral site surrounded by oxygen atoms. The lifetime of this photoexcited state is discussed.

Keywords Photoexcitation · Fe₂O₃ · TiO₂ · Visible light · CEMS

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✉ Taizo Kawauchi
kawauchi@iis.u-tokyo.ac.jp

Naoki Nagatsuka
naoki@iis.u-tokyo.ac.jp

Katsuyuki Fukutani
fukutani@iis.u-tokyo.ac.jp

¹ Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo, 153-8505, Japan

1 Introduction

TiO₂ is well known as a photocatalyst for a number of applications. Photoexcitation induces charge carriers, which play the role of oxidation and reduction [1, 2]. Since the band gap of TiO₂ is 3.2 eV, it is only sensitive to ultraviolet light, which limits its wider application. To achieve sensitivity in visible light wavelength, much effort has been done to dope various oxides and realize narrow band gap [3–6].

It has been shown that iron-oxides like Fe₂O₃ and Fe₂TiO₅ are effective for photocatalysis in the visible light range. Fe₂O₃ has a band gap of 2.2 eV, which has sensitivity to visible light [7]. The mechanism of visible light sensitivity of doped TiO₂ is generally interpreted as either electron trap or hole trap [8]. To investigate the real mechanism of the doping effect, it is necessary to observe the photoexcited state of iron-oxide. It is considered that a trivalent iron ion in alpha-hematite plays a main role of photo-excitation. Two excitation processes are theoretically proposed [9]. One process is that Fe³⁺ is excited by photon and Fe²⁺ and a hole are created. The other process is that Fe³⁺ is excited by photon and Fe⁴⁺ and an electron are created.

Despite this theoretical prediction, no experimental evidence for the excitation state of iron in hematite has been presented yet. The difficulty arises from in-situ observation of the charged state of Fe under visible light irradiation. In this work, we demonstrate in-situ observation of the photoexcitation of iron in iron-oxide on TiO₂ with conversion electron Mössbauer spectroscopy.

2 Experiment

The sample was prepared in ultrahigh vacuum (UHV). The substrate of rutile TiO₂(100) was initially sputtered by argon ion and heated at a temperature of 1473 K. After cleaning the sample surface, ⁵⁷Fe was deposited on the substrate at a substrate temperature of 973 K. The evaporation rate of iron was 0.01 nm/s and the total amount of deposited iron was 1 nm. Reflection high energy electron diffraction (RHEED) was observed before and after Fe deposition in UHV, to confirm the clean surface and crystal structure of the film.

The chemical states of iron on TiO₂ were investigated by X-ray photoelectron spectroscopy (XPS) with an Al K_α X-ray source. To investigate the chemical state of iron under light irradiation, we applied the conversion electron Mössbauer spectroscopy. The geometry is illustrated in Fig. 1. A Xe lamp was set at the opposite side of the gas flow proportional counter. Taking advantage that visible light transmits the TiO₂ substrate, light irradiated the sample through Pyrex glass. The gas for the proportional counter was four nine pure helium gas to avoid any reaction under light irradiation. By the air conditioner and a fan, the sample temperature was maintained below 300 K throughout the CEMS measurements. CEMS was measured before, under and after the light irradiation.

The visible light source used in the present study was a Xe lamp (type L2194 made by Hamamatsu Photonics K.K.). The intensity of light on the sample surface was about 0.3 W/cm² in this experiment. This value is about three times higher than the standard solar spectrum at an incidence angle of 42° on the earth surface, which is called air mass 1.5 global [10]. The ratio of ultraviolet ($\lambda < 370$ nm), visible ($370 < \lambda < 830$ nm) and infrared ($830 \text{ nm} < \lambda$) light is estimated to be 1, 63 and 36 %, respectively.

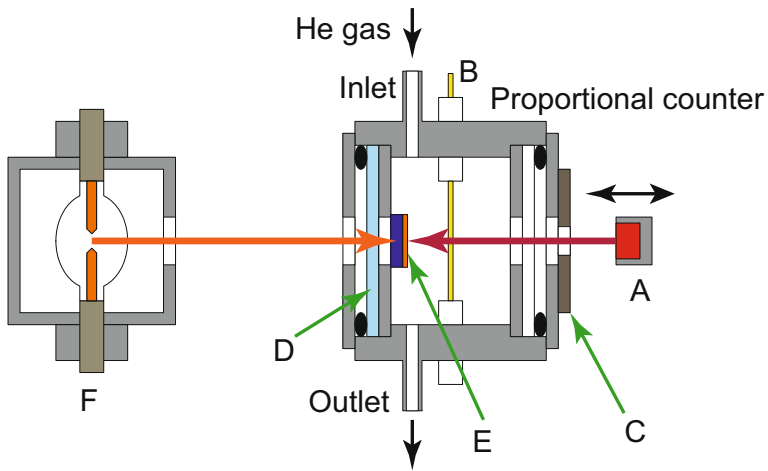


Fig. 1 Setup for conversion electron Mössbauer spectroscopy. A: ^{57}Co radioisotope, B: gold wire for the collector, C: Pb aperture with a diameter of 8mm, D: 2-mm-thick Pyrex glass, E: sample and F: Xe lamp

3 Result

3.1 RHEED

Figure 2a shows the RHEED pattern after cleaning of the surface, where clear sharp streaks can be seen. This indicates that some superstructures are formed parallel to the [010] direction on the $\text{TiO}_2(100)$ surface. Previous reports showed that three kinds of superstructures are formed along the [010] direction on the $\text{TiO}_2(100)$ surface [11]. It is also known that treatment of only sputtering and heating forms a surface mixed with all superstructures of 1×3 , 1×5 and 1×7 [12, 13]. In this work, we consider that the three superstructures coexist in a mixed manner on the surface of $\text{TiO}_2(100)$.

Figure 2b shows the RHEED pattern after evaporation of iron. It is likely that the surface is rough and the pattern reflects transmission diffraction. This RHEED pattern was reproducible for other samples after the same treatment. This indicates that an epitaxial layer was grown on the $\text{TiO}_2(100)$ surface. We should note that the diffraction spots are not symmetric with respect to the plane that is vertical to the surface and contains the [010] direction. Furthermore, the spot positions arrayed in square are not at a regular interval, and there are many spots at the position except for the corner of the square and the intersection of diagonal lines. In consideration of these features of the diffraction pattern, it is considered that $\alpha\text{-Fe}_2\text{O}_3$ was formed on the surface. In Fig. 2c, the calculated diffraction pattern expected for the rhombohedral $\text{Fe}_2\text{O}_3(0001)$ is shown. Though all calculated spots are not observed in Fig. 2b, the non-regular interval spot positions are in agreement with the experimental data. From the interval of the spots, the lattice constant of the rhombohedral phase of Fe_2O_3 is estimated to be compressed by about 7 % compared to that of the bulk α -hematite.

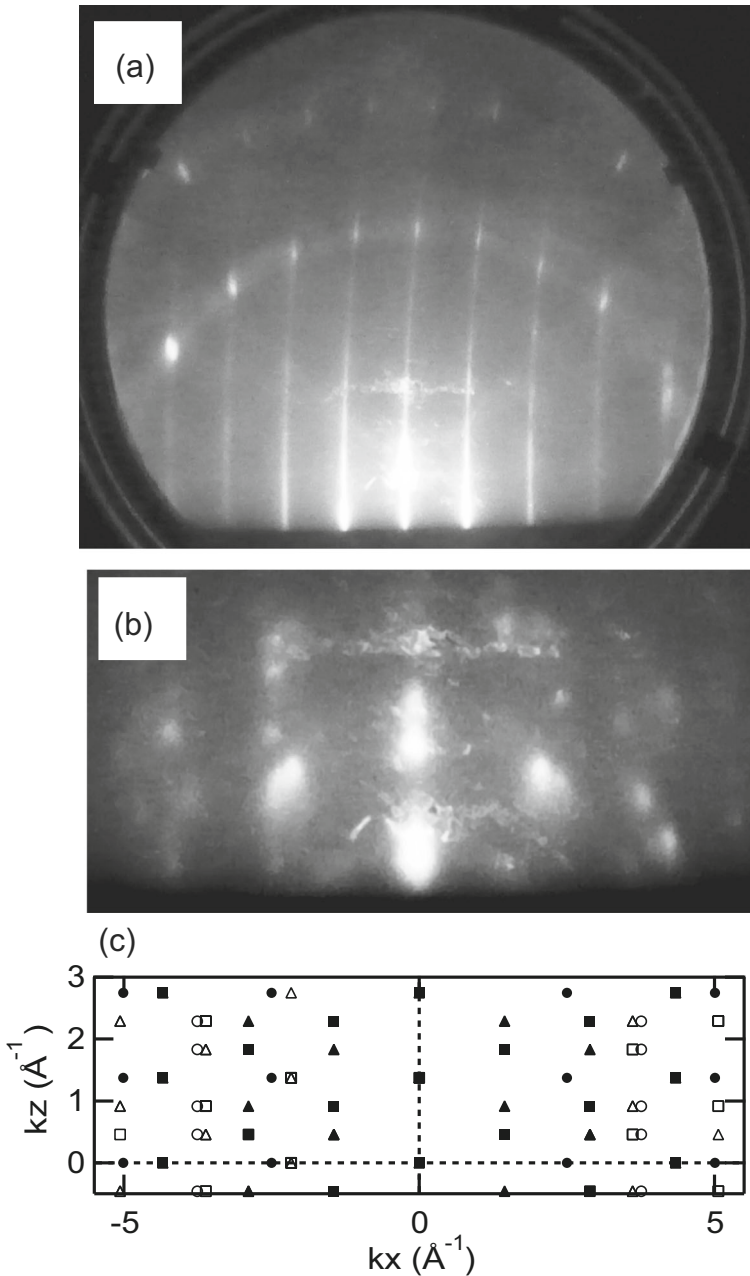


Fig. 2 RHEED patterns of (a) clean $\text{TiO}_2(100)$ surface and (b) after iron deposition. The direction of the electron beam is parallel to the $\text{TiO}_2[010]$ direction. (c) Calculated spots of the 0-th and first order Laue zones of $\text{Fe}_2\text{O}_3(0001)$. Filled circles, squares and triangles are spots in the 0-th order Laue zone in the direction of $[1\bar{1}00]$, $[11\bar{2}0]$ and $[\bar{1}\bar{1}\bar{2}0]$, respectively. Open circles, squares and triangles are spots in the first order Laue zone in the directions as with those of filled marks

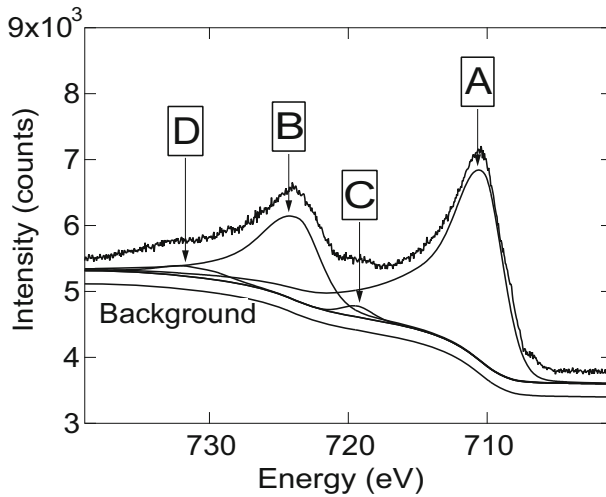


Fig. 3 XPS spectrum of the sample in the range of Fe2p. (a) and (b) are the peaks of Fe2p_{3/2} and Fe2p_{1/2}. (c) and (d) are satellite peaks of a and b, respectively

3.2 XPS

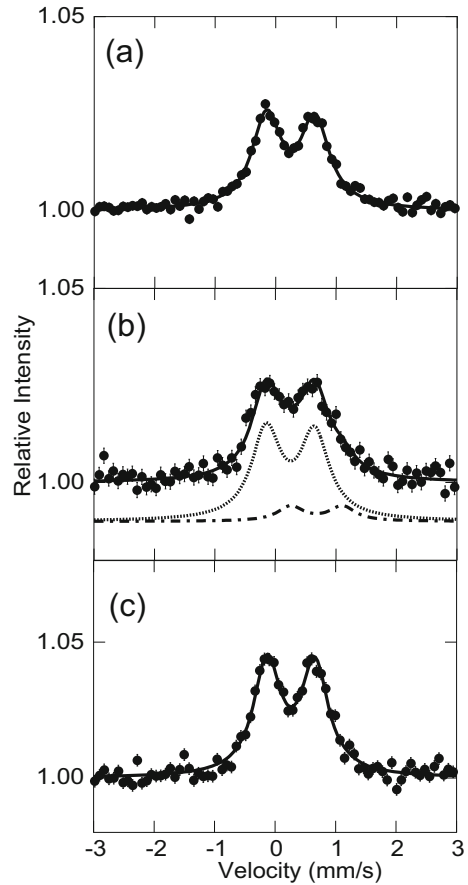
The result of XPS is shown in Fig. 3. Two peaks of Fe 2p spin-orbit states were observed at 710.3 and 724 eV. The component of α -Fe at 707 eV was hardly observed. Moreover, two satellite peaks of 719 and 739 eV were observed. These satellite peaks are well known as the characteristic shake-up peak of trivalent iron [14]. From these results, it is concluded that iron was oxidized to Fe³⁺, which is consistent with the RHEED result.

3.3 CEMS

The CEMS spectra are shown in Fig. 4. The spectrum in Fig. 4a reveals a quadrupole splitting. Under the light irradiation as shown in Fig. 4b, the spectrum became asymmetric with a tailing feature on the positive velocity side. Note that the dip between the double peak of the quadrupole splitting is shallow. As shown in Fig. 4c, the spectrum returned to the initial shape after the light irradiation. Before further discussion, we confirmed that the RHEED pattern was unchanged by the light irradiation in UHV, which means that the crystal structure of the iron-oxide was not influenced by the light irradiation. Hence, when fitting the spectrum in Fig. 4b, we considered that the initial component remained. Fitting was executed by fixing the parameters of the initial component except for the intensity and by adding an additional component with a quadrupole split. As a result, the other component with a large positive isomer-shift was estimated as shown in Fig. 4b. The intensity of the additional component to the original one in Fig. 4b is estimated to be 13 %.

As a result of fitting of the spectra in Fig. 4a, the values of the isomer-shift and quadrupole splitting were estimated to be $+0.25 \pm 0.001$ and 0.80 ± 0.01 mm/s, respectively. These values are in agreement with those of the superparamagnetic hematite in a previous study [15]. For the analysis of the spectrum in Fig. 4b on the other hand, the additional component

Fig. 4 CEMS spectra (a) before, (b) under and (c) after the light irradiation



has a large positive isomer shift of $+0.67 \pm 0.07$ mm/s with a similar quadrupole splitting of 0.85 ± 0.2 mm/s to that of the initial component. Taking into consideration that the crystal structure of Fe_2O_3 was unchanged by the light irradiation, it can be considered that the additional component corresponds to the excited state of the Fe^{3+} at the octahedral site in hematite. The values of the isomer-shift and the quadrupole splitting of this additional component are close to those of the Fe^{2+} at the octahedral site [16]. From these results, we consider that the photoexcited state by the light irradiation is the reduced state of Fe^{3+} in hematite.

We discuss the lifetime of the excited state. The flux of photons from the Xe lamp was $10^{18} \text{ cm}^{-2} \text{ s}^{-1}$. The absorption coefficient of hematite in the visible range is 10^9 cm^{-1} [17]. The effective iron-oxide thickness of the sample is about 3 nm, which corresponds to 10^{16} Fe atoms/ cm^2 . From these values, the photon absorption rate of an iron atom is estimated as $3 \times 10^4 \text{ s}^{-1}$. Since the experimental result shows that the ratio of the bivalent excited atom is 10 %, the lifetime of the excited state is about 3 μs . This value is sufficiently longer than the lifetime of the iron nuclear excited state.

4 Conclusion

By evaporating Fe on TiO₂, Fe₂O₃(0001) was epitaxially grown on TiO₂(100). By means of CEMS under dominantly visible light irradiation, we successfully observed a reduced state of Fe³⁺ in hematite as an excited state. Since the excited state is long-lived, Fe³⁺ in hematite on TiO₂ has potential as a catalyst for reduction.

References

1. Fujishima, A., Honda, K.: Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37 (1972)
2. Morisaki, H., Hariya, M., Yazawa, K.: Anomalous photoresonance of n-TiO₂ electrode in a photoelectrochemical cell. *Appl. Phys. Lett.* **30**, 7 (1977)
3. Sakthivel, S., Janczarek, M., Kisch, H.: Visible light activity and photoelectrochemical properties of nitrogen-doped TiO₂. *J. Phys. Chem. B* **108**, 19384 (2004)
4. Wang, X.H., Li, J.G., Kamiyama, H., Moriyoshi, Y., Ishigaki, T.: Wavelength-sensitive photocatalytic degradation of methyl orange in aqueous suspension over iron(III)-doped TiO₂ nanopowders under UV and visible light irradiation. *J. Phys. Chem. B* **110** (2006)
5. Lee, J.Y., Park, J., Cho, J.H.: Electronic properties of N- and C-doped TiO₂. *Appl. Phys. Lett.* **87**, 011904 (2005)
6. Han, C., Pelaez, M., Likodimos, V., Kontos, A.G., Falaras, P., O'Shea, K., Dionysiou, D.D.: Innovative visible light-activated sulfur doped TiO₂ films for water treatment. *Appl. Catal. B* **107**, 77 (2011)
7. Litter, M.I., Navio: Photocatalytic properties of iron-doped titania semiconductors. *J. Photochem. Photobiol. A* **98**, 171 (1996)
8. Xia, Y., Yin, L.: Core-shell structured α -Fe-Fe₂O₃@TiO₂ nanocomposites with improved photocatalytic activity in the visible light region. *Phys. Chem. Chem. Phys.* **15**, 18627 (2013)
9. Iordanova, N., Dupuis, M., Rosso, K.M.: Charge transport in metal oxide: a theoretical study of hematite α -Fe₂O₃. *J. Chem. Phys.* **122**, 144305 (2005)
10. Smestad, G.P., Krebs, F.C., Lampert, C.M., Chopra, K.L., Methew, X., Takakura, H.: Reporting solar cell efficiencies in solar energy materials and solar cells. *Solar Energy Mater. Solar Cells* **92**, 371 (2008)
11. Diebold, U.: The surface science of titanium dioxide. *Surf. Sci. Rep.* **48**, 53 (2009)
12. Murn, C.A., Hardman, R.J., Crouch, J.J., Raiker, G.N., Thornton, G.: Step and point defect effects on TiO₂(100) reactivity. *Surf. Sci.* **251/252**, 747 (1991)
13. Kunze, C., Torun, B., Giner, I., Grundmeier, G.: Surface chemistry and nonadecanoic acid adsorbate layers on TiO₂(100) surfaces prepared at ambient conditions. *Surf. Sci.* **606**, 1527 (2012)
14. Brudle, C.R., Chuang, T.J., Wandelt: Core valence level photoemission studies of iron oxide surfaces and the oxidation of iron. *Surf. Sci.* **68**, 459 (1977)
15. Kündig, W., Bömmel, H., Constabaris, Lindquist, R.H.: Some properties of supported small α -Fe₂O₃ particles determined with the Mössbauer effect. *Phys. Rev.* **142**, 327 (1966)
16. Gohy, C., Gérard, A., Grandjean, F.: Mössbauer study of wustite and manganese-wustite. *Phys. Stat. Sol. (a)* **74**, 583 (1982)
17. Glasscock, J.A., Barnes, P.R.F., Plumb, I.C., Bemdavid, A., Martin, P.J.: Structural, optical electrical properties of undoped polycrystalline hematite thin films produced using filtered arc deposition. *Thin Solid Films* **516**, 1716 (2008)