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**Mössbauer and Photocatalytic Studies of CaFe_2O_4
Nanoparticles-Containing Aluminosilicate prepared
from Domestic Waste Simulated Slag**

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Abstract

The relationship between local structure and visible-light activated photocatalytic effect of simulated domestic waste slag glass-ceramics (R-NaWSFe) was investigated. The largest pseudo-first-order rate constant of $9.75 \cdot 10^{-3} \text{ min}^{-1}$ was estimated for methylene blue decomposition test under the visible-light irradiation using R-NaWSFe with additional 30 mass% of Fe_2O_3 heat-treated at 900 °C for 100 min. The reason for the high photoactivity of this sample was mainly due to nanoparticles of CaFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ confirmed by the Mössbauer spectrum measured at 77 K. It is concluded that the nanoparticles of magnetic components in silica are essential for exhibiting visible-light activated catalytic effect.

Keywords

⁵⁷Fe Mössbauer spectroscopy, Photocatalytic effect, Visible-light, Nanoparticles, CaFe₂O₄, α -Fe₂O₃,

1. Introduction

Treatments of waste materials and wastewater are serious environmental problems all over the world. The Organization for Economic Co-operation and Development (OECD) reported that the annual total amount of municipal waste discarded from the OECD affiliated countries was calculated to be $6.22 \cdot 10^{11}$ kg, corresponding to the disposal of 560 kg/person in 2007 [1]. These reported values concerning the amounts of waste materials are almost stable as compared with those recently reported values of $6.56 \cdot 10^{11}$ kg, corresponding 522 kg/person reported in 2013 [2]. As for the wastewater pollution in Japan, chemical oxidation demand (COD) achievement rate, which indicates the ratio of closed water system like pond or lake having the COD value less than the upper limitation of 8 mg L⁻¹ has been stable at around 55 % [3]. These statistics show that the no effective solutions for reducing the waste materials and for wastewater purification have been developed. Therefore, finding a new route for recycling solid waste as water purifying material is essential for solving serious environmental problems.

Our research group found that the glass-ceramics prepared from a domestic waste slag (WS), of which chemical component is SiO₂(38.4 mass%), CaO(28.5), Al₂O₃(14.9), Fe₂O₃(5.5), and others (12.7), collected at the incineration plant in Ube city, Yamaguchi, Japan, with additional Fe₂O₃ decreased the COD value from 250 to 36 mg L⁻¹ after 10 days [4]. We then reported that iron-containing soda lime silicate glass with the chemical composition of 15Na₂O•15CaO•(70- x)SiO₂• x Fe₂O₃, abbreviated as NCFS x , with ‘ x ’ of 50 (in mass%) decreased COD value of artificial drain from 280 to 55.2 mg L⁻¹ after 10 days with the pseudo-first-order rate constant (k) of $4.7 \cdot 10^{-1}$ day⁻¹[5]. These results implied that the iron-silicate glass-ceramics could be applied as a water purifying materials for decomposing organic compounds which causes an increase in COD.

In relation to the development of wastewater purifying materials from iron silicate glass-ceramics, NCFS_x glass with ‘*x*’ of 50 heat-treated at 1000 °C for 100 min decomposed methylene blue (MB) in the aqueous solution with the *k* of $4.78 \cdot 10^{-4} \text{ min}^{-1}$ [6]. The room temperature (RT) Mössbauer spectrum of the heat-treated NCFS_x with ‘*x*’ of 50 were composed of an magnetic sextet with an isomer shift (δ) of 0.36 mm s^{-1} and an internal magnetic field (H_{int}) of 51.8 T due to hematite ($\alpha\text{-Fe}_2\text{O}_3$) and a relaxed sextet with the δ and H_{int} of 0.34 mm s^{-1} and 37.9 T, respectively, due to the iron oxide nanoparticles [6]. Further, a much larger *k* value of $9.26 \cdot 10^{-3} \text{ min}^{-1}$ was recorded for MB decomposition test using a heat-treated $15\text{Na}_2\text{O} \cdot 15\text{CaO} \cdot 40\text{Fe}_2\text{O}_3(30-x)\text{SiO}_2 \cdot x\text{Al}_2\text{O}_3$ glass, abbreviated as NCFSA_x with ‘*x*’ of 11 [7]. Two magnetic sextets with δ and H_{int} of 0.37 mm s^{-1} and 51.2 T and 0.38 mm s^{-1} and 52.4 T were observed from the RT Mössbauer spectrum of this sample [7].

Recently, a glass-ceramics prepared from Na_2CO_3 , WS and Fe_2O_3 , abbreviated as NaWSF_x, by melt-quenching method showed the *k* value of $2.65 \cdot 10^{-3} \text{ min}^{-1}$ when they were heat-treated at 800 °C for 100 min [8]. The Mössbauer spectra measured at 77 K showed several sextets, one of which had δ and H_{int} of 0.41 mm s^{-1} and 52.7 T attributed to nanoparticles of $\alpha\text{-Fe}_2\text{O}_3$ [8]. These results show that the iron-containing silicates exhibit photocatalytic ability through the presence of $\alpha\text{-Fe}_2\text{O}_3$ and its analogous iron oxides at the nano-scale. However, it is difficult for NaWSF_x to precisely evaluate the visible light-activated photocatalytic effect of $\alpha\text{-Fe}_2\text{O}_3$ precipitated in the silica glass matrix because WS contains lots of impurity elements.

Therefore, in order to classify the chemical environment of iron oxides which causes the visible-light activated photocatalytic activity in the silica matrix, the relationship between visible-light activated catalytic effects and local structure of “*simulated*” domestic waste slag with different iron concentrations, abbreviated as R-NaWSF_x (*x* = 10, 30 and 50 mass% of Fe_2O_3 in the $\text{Na}_2\text{O}\text{-CaO}\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system) was investigated by ^{57}Fe -Mössbauer spectroscopy, X-ray diffractometry(XRD), and ultraviolet-visible light absorption spectroscopy(UV-Vis).

2. Experimental

Glass and ceramics produced from domestic waste model slag with different iron concentration, denoted as model-slag+10Na₂O+xFe₂O₃, abbreviated as (R-NaWSF_x, $x = 10, 30, 50$ mass%) were prepared by melt quenching method. The chemical composition of the model slag was based on the previously reported values[8] except for minor components of the first transition metal oxides. Weighed amounts of Na₂CO₃ (Wako 199-01585), CaCO₃ (Wako 030-00385), Fe₂O₃ (Wako 096-04825), Al(OH)₃ (Wako 014-01925) and SiO₂ (Kanto Kagaku 37974-00) were mixed with an agate mortar. The mixture was put into a platinum crucible and melted at 1400 °C for 60 min in an electrical muffle furnace. Dark brown samples were obtained by dipping the crucible bottom into ice-cold water. The prepared glass and glass-ceramics were subjected to the following isothermal heat treatment for 100 min at 800 and 900 °C. The estimated chemical composition of R-NaWSF_x is listed in Table 1.

Table 1 The estimated chemical composition of R-NaWSF_x (in wt%)

x	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
10	11.2	26.9	14.0	23.3	24.6
30	9.6	23.1	12.0	20.0	35.3
50	8.4	20.2	10.5	17.5	43.4

The prepared glasses and glass-ceramics containing model slag plus additions, before and after heat-treatment were characterized by X-ray diffractometry (XRD), ⁵⁷Fe-Mössbauer spectroscopy and ultra-violet visible-light absorption spectroscopy (UV-VIS). The XRD patterns were measured in the 2θ range of 10 and 80 ° with the sampling pitch of 0.02 ° and scan speed of 5 ° min⁻¹. The X-rays of Cu-K_α ($\lambda = 0.1541$ nm) were generated by applying the voltage of 50 kV and the current of 300 mA. The recorded XRD patterns were identified by JCPDS cards by PDXL. Measurements of Mössbauer

spectra at room and liquid nitrogen temperatures (77 K) were carried out by conventional acceleration method using 925MBq $^{57}\text{Co}(\text{Rh})$ and $\alpha\text{-Fe}$ as a source and reference, respectively. For the measurement, 100 mg of well-pulverized sample is homogeneously dispersed on the transparent adhesive tape so that it was circular in shape with a diameter of 10 mm. The obtained spectra were fitted by Lorentzian lineshapes using Mosswinn 3.0i XP software. For the evaluation of visible-light activated photocatalytic ability, 20 mL of $20\ \mu\text{mol L}^{-1}$ methylene blue aqueous solution (MB_{aq}) prepared from methylene blue (Wako 133-06962) was poured into a plastic vial together with 40 mg of powdered sample, and irradiated with the visible light with the wavelength of 420 – 700 nm emitted from a metal halide lamp with an output power of 100 W and intensity of $6\ \text{mWcm}^{-2}$. The MB_{aq} concentration after the catalytic reaction was determined by UV-VIS spectrometer under the wavelength range of 200 – 800 nm and a scan speed of $1\ \text{nm sec}^{-1}$.

3. Results and discussion

3.1 UV-VIS Spectra

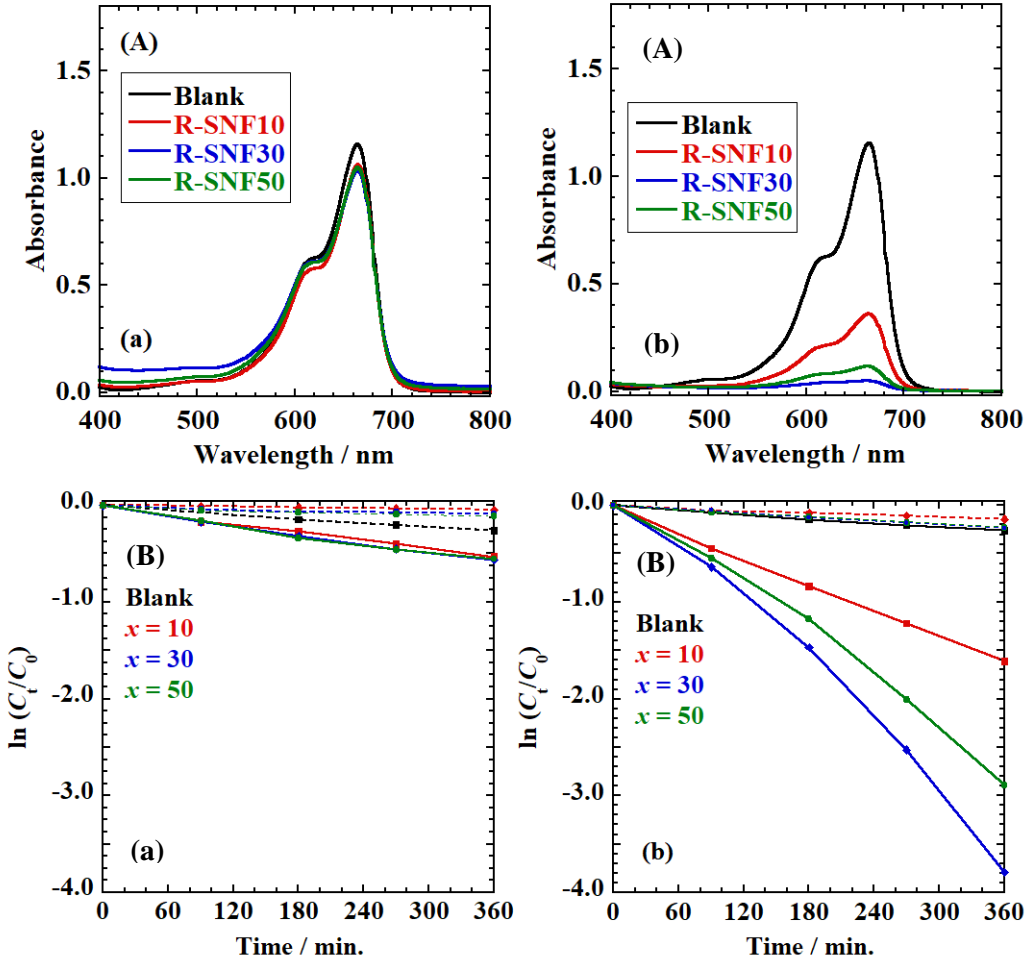


Fig. 1 (A) UV–Vis spectra and (B) $\ln(C_t/C_0)$ vs. t plot of MB_{aq} reacted with R-NaWSFex after heat treatment for 100 min. at (a) 800 and (b) 900 °C

UV-Vis spectra of MB_{aq} degradation test using R-NaWSFex with ‘x’ of 10, 30 and 50 heat-treated for 100 min at 800 and 900 °C are shown in Fig. 1. We could confirm the maximum absorption wavelength at 664 nm due to the original MB from the UV-Vis spectra before the degradation test. The concentration of the MB_{aq} was determined by the Lambert-Beer equation, *i.e.*,

$$A = \varepsilon_0 C_t l \quad (1)$$

where A , ε_0 , C_t and l are absorbance determined at 664 nm, molar absorption coefficient ($= 7.9 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}[9]$), MB concentration after t min [mol L^{-1}] and cell length ($= 1$ cm), respectively. When the MB_{aq} was reacted in the dark with R-NaWSFex with x of 10,

30 and 50 after heat-treated at 800 °C for 100 min, almost constant MB concentration was recorded for the degradation test using all three samples as shown in the dotted lines in Fig. 1 (B) (a). On the other hand, a decrease in MB concentration was observed from 20.0 to 11.8, 11.4, and 12.8 $\mu\text{mol L}^{-1}$ reacted under the visible-light with R-NaWSFex having the 'x' of 10, 30 and 50 for 360 min, respectively (see Fig. 1 (B) (a)). However, the MB concentration after 360 min irradiation of visible-light was comparable to that of a blank test (12.8 $\mu\text{mol L}^{-1}$). In contrast, remarkable decreases in MB concentration were observed from 20 to 4.00, 0.45, and 1.10 $\mu\text{mol L}^{-1}$ by using R-NaWSFex with 'x' of 10, 30 and 50 heat-treated at 900 °C, respectively (see Fig. 1 (B) (b)).

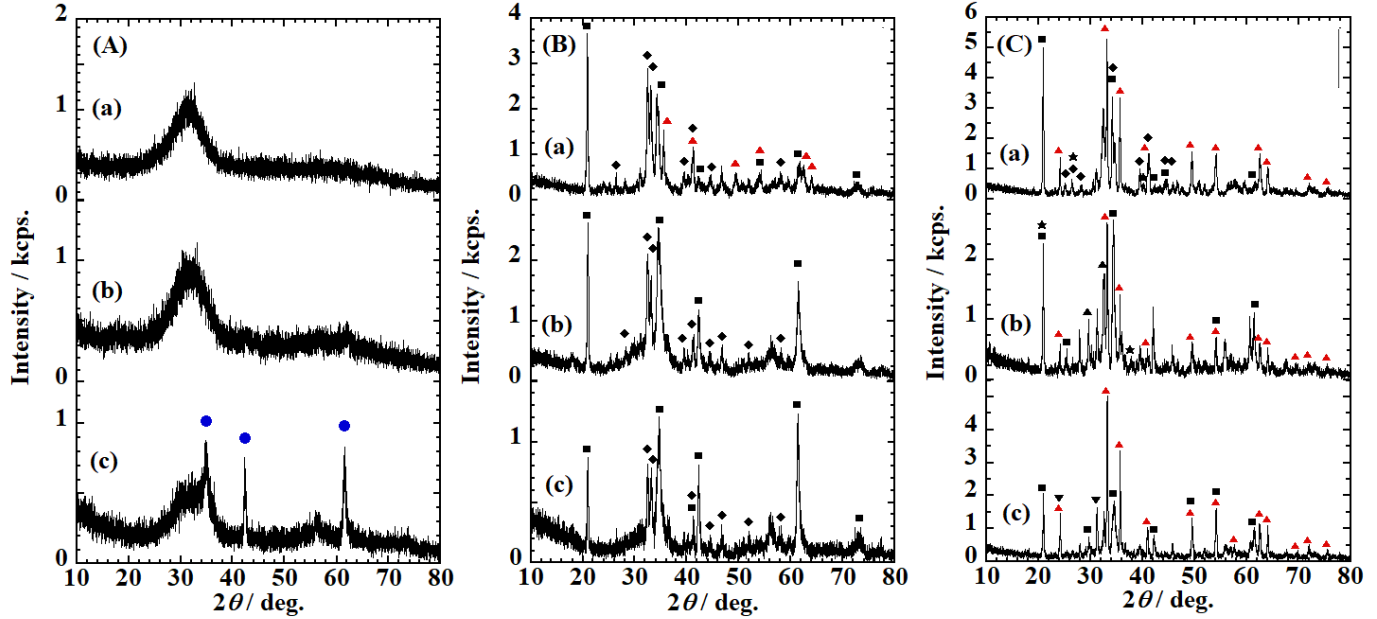
A pseudo-first-order rate constant (k) is evaluated by the following equation, *i.e.*,

$$\ln(C/C_0) = -kt \quad (2)$$

where C_0 is the initial MB concentration (= 20 $\mu\text{mol L}^{-1}$). In order to evaluate the photocatalytic ability of the studied samples, estimation of k values is carried out by plotting, $\ln(C/C_0)$ vs. t , as shown in Fig. 1(B). Under visible-light irradiation, almost comparable k values of $(1.48 \pm 0.02) \cdot 10^{-3}$, $(1.63 \pm 0.01) \cdot 10^{-3}$ and $(1.64 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1}$ were respectively obtained for R-NaSWFex with 'x' of 10, 30 and 50 heat-treated for 100 min at 800 °C, which is slightly larger than that of blank value (= $(1.20 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1}$). In contrast, much larger k values of $(4.52 \pm 0.01) \cdot 10^{-3}$, $(9.75 \pm 0.01) \cdot 10^{-3}$ and $(7.59 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1}$ were estimated for the same samples heat-treated for 100 min at 900 °C under the visible-light irradiation. These results indicate that R-NaWSFex heat-treated at the higher temperature has a higher photocatalytic ability which depends on kinds and amounts of the precipitated crystalline phases. In our previous study, we could observe a k value of $2.65 \cdot 10^{-3} \text{ min}^{-1}$ for a glass-ceramics prepared from Na_2O +domestic waste slag+ $x\text{Fe}_2\text{O}_3$ by melting at 1400 °C for 1 h and heat-treated at 800 °C for 100 min [8]. By comparing the largest k value obtained for R-NaWSFe30 heat-treated at 900 °C in this study(= $9.75 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1}$) and that obtained for the glass-ceramics prepared from existing domestic waste slag(= $2.65 \cdot 10^{-3} \text{ min}^{-1}$), it can be said that much more effective photocatalytic material can be prepared by isolating impurity from existing domestic waste slag.

157

158 3.2 XRD patterns



159 **Fig. 2** XRD patterns of R-NaWSF_x samples with 'x' of (a)10, (b) 30 and (c) 50, (A)
 160 before and after heat treatment for 100 min at (B) 800 °C and (C) 900 °C. ●: γ-Fe₂O₃,
 161 ■: NaAlSiO₄, ◆: Ca₂SiO₄, ▲: α-Fe₂O₃, ▲: Ca₃SiO₅, ▼: Ca₂Al₂SiO₇, ★: SiO₂.

162 In Fig. 2, XRD patterns of R-NaWSF_x samples before and after heat treatment for 100
 163 min at 800 °C and 900 °C are indicated. Before the heat treatment, we could confirm X-
 164 ray halo patterns which have a peak at 2θ of around 32.0° due to the amorphous structure
 165 for R-NaWSF_x samples with 'x' of 10 and 30, whereas sharp intense peaks were
 166 detected at the 2θ of 34.8 , 42.3 and 61.5° due to maghemite (γ-Fe₂O₃, PDF No. 01-076-
 167 4113) for R-NaWSFe50. The crystallite size (D) of compounds detected by the XRD
 168 patterns can be estimated by Sherrer's formula [10], *i.e.*,

$$169 \quad D = K\lambda / \beta \cos\Theta \quad (3)$$

170 where K , λ and β are Sherrer's constant, wavelength of the X-ray(= 0.1541 nm) and
 171 full width at the half of maximum, respectively. Using the Sherrer's formula (3), the
 172 crystallite size of γ-Fe₂O₃ precipitated in R-NaWSFe50 was calculated to be (24 ± 9) nm.

It should be noted that the thermal stability of R-NaWSFex becomes higher because XRD pattern of glass-ceramics prepared from as collected domestic waste slag with similar chemical composition showed peaks due to the crystalline phase when it contains additional Fe₂O₃ of more than 30 mass% [8]. As for XRD patterns of R-NaWSFex samples after heat-treatment at 800 °C, crystalline phases of NaAlSiO₄ (PDF No. 00-011-0221) and Ca₂SiO₄ (PDF No. 01-086-0399) were identified in all samples, while α-Fe₂O₃ (PDF No. 01-089-0599) can be identified only in the case of $x = 10$. After heat-treatment at 900 °C, α-Fe₂O₃ can be detected in all samples with additional phases of SiO₂ (PDF No. 01-089-8937) for $x = 10$ and 30, while for $x = 50$, Ca₂Al₂SiO₇ (PDF No. 01-075-1677) can be detected. The averaged crystallite sizes were respectively estimated to be 29 ± 4 , 35 ± 5 and 25 ± 3 nm for $x = 10$, 30 and 50 heat-treated at 800 °C, while they were 47 ± 5 , 44 ± 4 and 41 ± 3 nm for 900 °C heat-treated samples. When we consider the differences in the k values of $1.48\text{--}1.64 \cdot 10^{-3} \text{ min}^{-1}$ observed for MB_{aq} degradation test using R-NaWSFex heat-treated at 800 °C and those of $4.52 \cdot 10^{-3}$ – $9.75 \cdot 10^{-3} \text{ min}^{-1}$ recorded by using samples after heat-treated at 900 °C, it can be considered that precipitation of α-Fe₂O₃ phase is essential for exhibiting visible-light activated photocatalytic effect of heat-treated R-NaWSFex.

3.3 ⁵⁷Fe-Mössbauer Spectra

3.3.1 Room temperature (RT) ⁵⁷Fe-Mössbauer Spectra

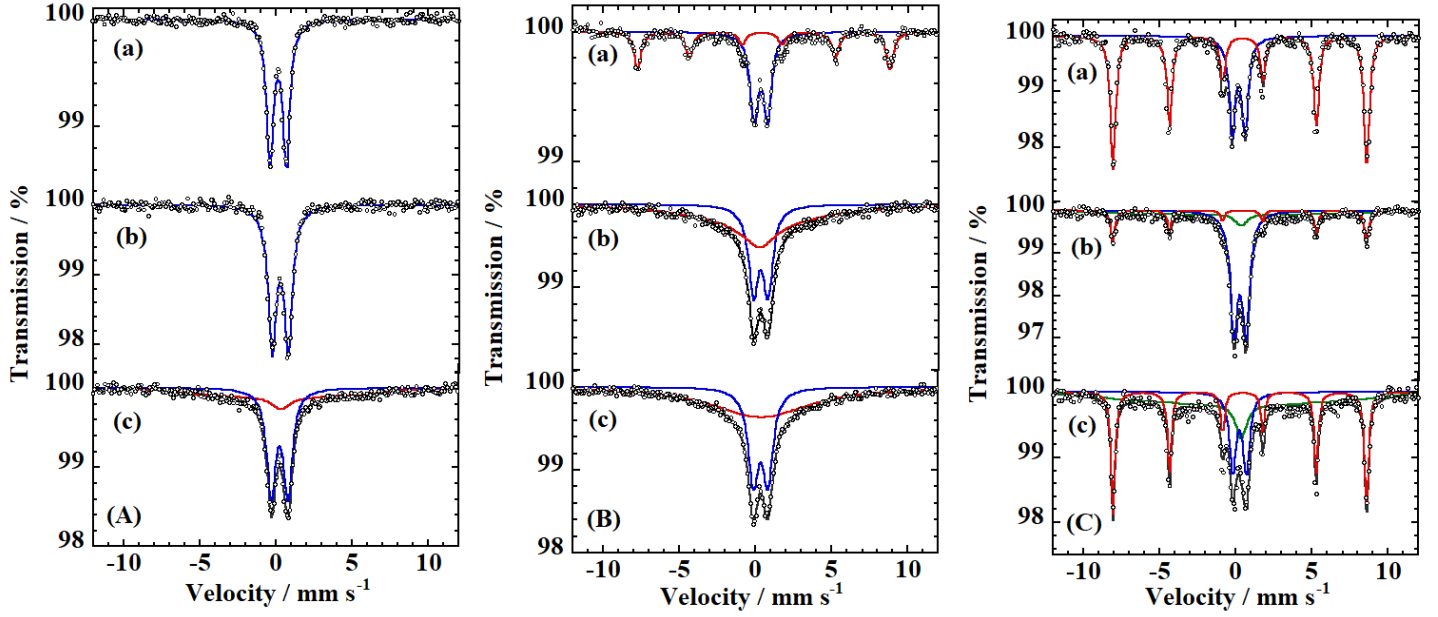


Fig. 3 RT Mössbauer spectra of R-NaWSF_x sample with 'x' of (a) 10, (b) 30, and (c) 50
(A) before and after heat treatment for 100 min at (B) 800 °C, and (C) 900 °C

Table 2 ⁵⁷Fe-Mössbauer parameters of R-NaWSF_x sample with 'x' of 10, 30, 50 before
and after heat treatment for 100 min at 800 °C, and 900 °C for 100 min

	x	Assignment	A %	δ mm s^{-1}	Δ mm s^{-1}	H_{int} T	Γ mm s^{-1}
Before	10	$\text{Fe}^{\text{III}}(T_d)$	100	$0.15_{\pm 0.01}$	$1.06_{\pm 0.01}$	—	$0.55_{\pm 0.01}$
	30	$\text{Fe}^{\text{III}}(T_d)$	100	$0.29_{\pm 0.01}$	$1.04_{\pm 0.01}$	—	$0.64_{\pm 0.01}$
	50	$\text{Fe}^{\text{III}}(T_d)$	59.5	$0.25_{\pm 0.01}$	$1.10_{\pm 0.02}$	—	$0.68_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(O_h)\text{M}$	40.5	$0.37_{\pm 0.01}$	$0.00_{\pm 0.01}$	$37.0_{\pm 2.6}$	$0.99_{\pm 0.30}$
800	10	$\text{Fe}^{\text{III}}(T_d)$	56.3	$0.34_{\pm 0.01}$	$0.88_{\pm 0.01}$	—	$0.62_{\pm 0.01}$
		$\text{Fe}^{\text{III}}(O_h)$	43.7	$0.49_{\pm 0.01}$	$0.10_{\pm 0.02}$	$51.4_{\pm 0.1}$	$0.54_{\pm 0.03}$
	30	$\text{Fe}^{\text{III}}(T_d)$	38.3	$0.34_{\pm 0.01}$	$0.95_{\pm 0.01}$	—	$0.76_{\pm 0.03}$
		$\text{Fe}^{\text{III}}(T_d)$	61.7	$0.27_{\pm 0.12}$	$0.00_{\pm 0.01}$	$48.0_{\pm 0.1}$	$1.83_{\pm 0.88}$
	50	$\text{Fe}^{\text{III}}(T_d)$	38.2	$0.34_{\pm 0.01}$	$0.95_{\pm 0.01}$	—	$0.82_{\pm 0.03}$
		$\text{Fe}^{\text{III}}(T_d)$	61.8	$0.37_{\pm 0.01}$	$0.00_{\pm 0.01}$	$48.2_{\pm 0.1}$	$7.71_{\pm 0.96}$
900	10	$\text{Fe}^{\text{III}}(T_d)$	30.3	$0.19_{\pm 0.01}$	$0.83_{\pm 0.01}$	—	$0.49_{\pm 0.01}$

		$\text{Fe}^{\text{III}}(\text{O}_\text{h})\text{H}$	69.7	$0.38_{\pm 0.01}$	$-0.20_{\pm 0.01}$	$51.6_{\pm 0.02}$	$0.40_{\pm 0.01}$
	30	$\text{Fe}^{\text{III}}(\text{T}_\text{d})$	58.1	$0.29_{\pm 0.01}$	$0.78_{\pm 0.01}$	—	$0.58_{\pm 0.01}$
		$\text{Fe}^{\text{III}}(\text{O}_\text{h})\text{H}$	16.3	$0.37_{\pm 0.01}$	$-0.20_{\pm 0.01}$	$51.7_{\pm 0.05}$	$0.30_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(\text{O}_\text{h})\text{H}$	25.6	$0.37_{\pm 0.01}$	$-0.20_{\pm 0.01}$	$51.2_{\pm 0.01}$	$0.29_{\pm 0.01}$
		$\text{Fe}^{\text{III}}(\text{T}_\text{d})$	20.1	$0.26_{\pm 0.01}$	$0.89_{\pm 0.02}$	—	$0.51_{\pm 0.03}$
	50	$\text{Fe}^{\text{III}}(\text{O}_\text{h})\text{H}$	37.3	$0.38_{\pm 0.01}$	$-0.20_{\pm 0.01}$	$51.7_{\pm 0.02}$	$0.31_{\pm 0.01}$
		$\text{Fe}^{\text{III}}(\text{O}_\text{h})\text{H}$	42.6	$0.37_{\pm 0.01}$	$-0.20_{\pm 0.01}$	$50.2_{\pm 1.91}$	$0.31_{\pm 0.07}$

198 A: absorption area (± 0.5 %), M: $\gamma\text{-Fe}_2\text{O}_3$, H: $\alpha\text{-Fe}_2\text{O}_3$

199

200 ^{57}Fe -Mössbauer spectra recorded at room temperature and the corresponding
201 parameters of R-NaWSFex sample before and after heat-treatment for 100 min at 800 °C
202 and 900 °C were shown in Fig. 3 and Table 2, respectively. As shown in Fig. 3 (A) (a)-
203 (c), ^{57}Fe -Mössbauer spectra of R-NaWSFex before the heat treatment are composed of
204 one paramagnetic doublet with an isomer shift (δ) of $(0.15 \pm 0.01) - (0.25 \pm 0.01) \text{ mm s}^{-1}$
205 1 and quadrupole splitting (Δ) of $(1.04 \pm 0.01) - (1.10 \pm 0.02) \text{ mm s}^{-1}$ due to distorted
206 $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra. An additional relaxed component with δ of $(0.37 \pm 0.01) \text{ mm s}^{-1}$ and
207 an internal magnetic field (H_{int}) of $(37.0 \pm 2.6) \text{ T}$ due to iron oxide nanoparticles was
208 observed for R-NaWSFe50 (Fig. 3 (A) (c)). The ^{57}Fe -Mössbauer spectrum of R-
209 NaWSFe10 after heat treatment for 100 min at 800 °C indicated one paramagnetic
210 doublet due to distorted $\text{Fe}^{\text{III}}\text{O}_4$ and a magnetic sextet with δ of $(0.49 \pm 0.01) \text{ mm s}^{-1}$, H_{int}
211 of $(51.4 \pm 0.1) \text{ T}$ and Γ of $(0.54 \pm 0.03) \text{ mm s}^{-1}$ due to regular $\alpha\text{-Fe}_2\text{O}_3$. A sextet with
212 similar parameters attributed to $\alpha\text{-Fe}_2\text{O}_3$ were observed for all the Mössbauer of R-
213 NaWSFex heat-treated at 900 °, as shown in Fig. 3 (C) (a)-(c). These results are
214 consistent with those of corresponding XRD patterns. However, there are several
215 components which are not clearly identified for the crystalline phase of iron oxide.
216 Therefore, low-temperature Mössbauer measurement was required in order to
217 characterize these components.

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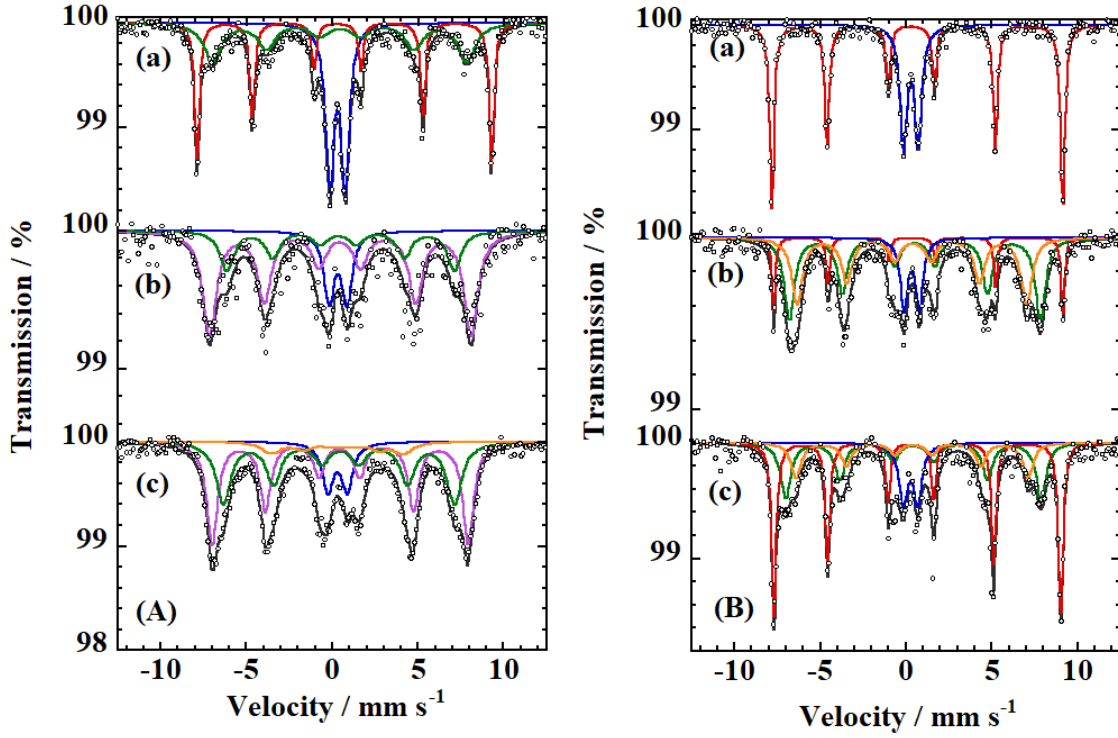
219 3.3.2 LNT ^{57}Fe -Mössbauer Spectra

Fig. 4 Mössbauer spectra measured at 77 K of R-NaWSFex sample with 'x' of (a) 10, (b) 30 and (c) 50 after heat treatment for 100 min at (A) 800 °C and (B) 900 °C

Table 3 Mössbauer parameters at 77 K of R-NaWSFex sample after heat treatment for 100 min at 800 °C and 900 °C

	x	Assignment	A %	δ mm s^{-1}	Δ mm s^{-1}	H_{int} T	Γ mm s^{-1}
800	10	$\text{Fe}^{\text{III}}(T_d)$	32.1	$0.29_{\pm 0.01}$	$0.90_{\pm 0.01}$	—	$0.56_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(O_h)\text{H}$	34.9	$0.49_{\pm 0.01}$	$0.39_{\pm 0.01}$	$53.4_{\pm 0.1}$	$0.33_{\pm 0.01}$
		$\text{Fe}^{\text{III}}(O_h)$	33.0	$0.44_{\pm 0.03}$	$-0.04_{\pm 0.06}$	$46.1_{\pm 0.1}$	$1.20_{\pm 0.10}$
	30	$\text{Fe}^{\text{III}}(T_d)$	15.2	$0.32_{\pm 0.03}$	$1.04_{\pm 0.05}$	—	$0.70_{\pm 0.10}$
		$\text{Fe}^{\text{III}}(O_h)\text{C}$	61.8	$0.44_{\pm 0.02}$	$0.03_{\pm 0.04}$	$47.4_{\pm 0.1}$	$0.95_{\pm 0.07}$
		$\text{Fe}^{\text{III}}(T_d)$	23.1	$0.42_{\pm 0.05}$	$0.13_{\pm 0.01}$	$41.1_{\pm 0.05}$	$0.95_{\pm 0.02}$
	50	$\text{Fe}^{\text{III}}(T_d)$	10.7	$0.31_{\pm 0.02}$	$1.12_{\pm 0.04}$	—	$0.77_{\pm 0.06}$
		$\text{Fe}^{\text{III}}(O_h)\text{C}$	45.0	$0.43_{\pm 0.01}$	$0.03_{\pm 0.02}$	$46.4_{\pm 0.1}$	$0.75_{\pm 0.04}$

		$\text{Fe}^{\text{III}}(T_d)$	36.2	$0.43_{\pm 0.02}$	$-0.10_{\pm 0.04}$	$41.9_{\pm 0.2}$	$1.01_{\pm 0.07}$
		$\text{Fe}^{\text{III}}(T_d)$	8.1	$0.43_{\pm 0.01}$	$-0.22_{\pm 0.24}$	$24.0_{\pm 0.7}$	$1.27_{\pm 0.4}$
900	10	$\text{Fe}^{\text{III}}(T_d)$	32.7	$0.28_{\pm 0.01}$	$0.86_{\pm 0.01}$	-	$0.48_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(O_h)H$	67.3	$0.47_{\pm 0.01}$	$0.35_{\pm 0.01}$	$52.7_{\pm 0.1}$	$0.32_{\pm 0.01}$
	30	$\text{Fe}^{\text{III}}(T_d)$	12.1	$0.33_{\pm 0.02}$	$0.90_{\pm 0.03}$	-	$0.50_{\pm 0.04}$
		$\text{Fe}^{\text{III}}(O_h)H$	13.0	$0.52_{\pm 0.01}$	$0.37_{\pm 0.02}$	$52.4_{\pm 0.1}$	$0.25_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(O_h)C$	40.5	$0.51_{\pm 0.01}$	$-0.01_{\pm 0.02}$	$45.5_{\pm 0.1}$	$0.71_{\pm 0.05}$
		$\text{Fe}^{\text{III}}(T_d)$	34.4	$0.37_{\pm 0.02}$	$-0.08_{\pm 0.03}$	$41.5_{\pm 0.2}$	$0.75_{\pm 0.06}$
	50	$\text{Fe}^{\text{III}}(T_d)$	12.6	$0.26_{\pm 0.03}$	$0.84_{\pm 0.04}$	-	$0.60_{\pm 0.07}$
		$\text{Fe}^{\text{III}}(O_h)H$	42.1	$0.46_{\pm 0.01}$	$0.38_{\pm 0.01}$	$52.0_{\pm 0.1}$	$0.32_{\pm 0.02}$
		$\text{Fe}^{\text{III}}(O_h)C$	27.7	$0.44_{\pm 0.02}$	$-0.02_{\pm 0.05}$	$46.3_{\pm 0.2}$	$0.69_{\pm 0.07}$
		$\text{Fe}^{\text{III}}(T_d)$	17.6	$0.39_{\pm 0.04}$	$-0.10_{\pm 0.07}$	$42.0_{\pm 0.1}$	$0.69_{\pm 0.07}$

225 A: absorption area ($\pm 0.5\%$), H: $\alpha\text{-Fe}_2\text{O}_3$, C: CaFe_2O_4

226 ^{57}Fe -Mössbauer spectra measured at 77 K and the corresponding parameters for R-
227 NaWSFex sample with 'x' of 10, 30 and 50 heat-treated for 100 min at 800 °C and 900 °C
228 are indicated in Fig. 4 and Table 3, respectively. When in the case of the 77 K ^{57}Fe -
229 Mössbauer spectrum of R-NaSWFe10 heat-treated at 800 °C, one paramagnetic doublet
230 with δ of (0.29 ± 0.01) mm s $^{-1}$ and Δ of (0.90 ± 0.01) mm s $^{-1}$ due to $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra
231 substituting for $\text{Si}^{\text{IV}}\text{O}_4$, and two sextets with δ and H_{int} of (0.49 ± 0.01) mm s $^{-1}$ and $(53.4$
232 $\pm 0.1)$ T due to $\alpha\text{-Fe}_2\text{O}_3$, and (0.44 ± 0.03) mm s $^{-1}$ and (46.1 ± 0.1) T iron oxide
233 nanoparticles were observed. It is noted that the positive Δ value of (0.39 ± 0.01) mm s $^{-1}$
234 observed for 77 K Mössbauer spectrum of R-NaWSFe10 is due to Morin transition
235 occurred at 260 K[11], which is also confirmed for 77 K Mössbauer spectrum of R-
236 NaWSFe heat-treated at 900 °C indicating the existence of $\alpha\text{-Fe}_2\text{O}_3$ in the XRD patterns
237 (Fig. 2 (C)). In addition to a paramagnetic component and two magnetic sextets observed
238 in the 77 K Mössbauer spectrum of R-NaWSFe10, additional one sextet was observed for
239 LNT Mössbauer spectrum of NaWSFe30, and two sextets for NaWSFe50, respectively.

On the other hand, a paramagnetic doublet with δ of $(0.26 \pm 0.03) - (0.33 \pm 0.02) \text{ mm s}^{-1}$ and Δ of $(0.84 \pm 0.04) - (0.90 \pm 0.03) \text{ mm s}^{-1}$ due to $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra and a magnetic sextet with δ of $(0.46 \pm 0.01) - (0.51 \pm 0.02) \text{ mm s}^{-1}$, internal magnetic field (H_{int}) of $(52.0 \pm 0.1) - (52.7 \pm 0.1) \text{ T}$ and line width (I) of $(0.25 \pm 0.02) - (0.32 \pm 0.02) \text{ mm s}^{-1}$ due to $\alpha\text{-Fe}_2\text{O}_3$ were commonly found for Mössbauer spectra of R-NaWSFex heat-treated at 900 °C measured at 77 K. The larger H_{int} value obtained in this study is caused by weak ferromagnetic interaction due to lowering of Morin transition temperature. A similar Mössbauer spectrum with δ of 0.49 mm s^{-1} and H_{int} of 53.5 T measured at 4.2 K was previously reported for $\alpha\text{-Fe}_2\text{O}_3$ with the particle size of smaller than 20 nm [12]. In addition to these two components, two magnetic sextets with δ and H_{int} of $(0.51 \pm 0.01) \text{ mm s}^{-1}$ and $(45.5 \pm 0.1) \text{ T}$ due to CaFe_2O_4 [13], and $(0.37 \pm 0.02) \text{ mm s}^{-1}$ and $(41.5 \pm 0.2) \text{ T}$ due to iron oxide nanoparticles with unknown structure are observed for 77 K Mössbauer spectrum of R-NaWSFe30 heat-treated at 900 °C. Smaller absorption area (A) of 27.7 % due to CaFe_2O_4 and 17.6 % of unknown iron oxide nanoparticles were observed for 77 K Mössbauer spectrum of R-NaWSFe50 heat-treated at 900 °C. In the evaluation of k values for the MB decomposition by using heat-treated R-NaWSFex, the largest value of $(9.75 \pm 0.01) \cdot 10^{-3} \text{ min}^{-1}$ was obtained when R-NaWSFe30 heat-treated at 900 °C was used. It was reported that the band gap energy of CaFe_2O_4 of 1.85-1.90 eV [14,15] is slightly smaller than that of $\alpha\text{-Fe}_2\text{O}_3$ (1.9-2.2 eV) [16,17]. By considering together this information with the above-described results of Mössbauer and UV-Vis studies, it can be said that the existence of nanoparticles of CaFe_2O_4 cause the increase of k value in addition to $\alpha\text{-Fe}_2\text{O}_3$. It is concluded that iron oxide nanoparticles precipitated in aluminosilicate are essential for exhibiting visible-light activated photocatalytic effect.

Conclusions

The largest pseudo-first-order rate constant (k) of $9.75 \cdot 10^{-3} \text{ min}^{-1}$ was recorded for methylene blue degradation test by using R-NaWSFe30 heat-treated at 900 °C for 100 min under visible-light irradiation. 77 K ^{57}Fe -Mössbauer spectrum of this sample

revealed the existence of nanoparticles of CaFe_2O_4 , which was essential for the visible-light activated photocatalytic effect. It is concluded that visible-light activated photocatalyst can be prepared from ubiquitous elements of Na, Al, Si, O, Ca, and Fe. This paper implies that solid waste such as domestic slag which contains above-described elements can be recycled as wastewater purifying material in the future.

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References

- [1] OECD (2010) "Municipal waste" in OECD Factbook 2010: Economic, Environmental and Social Statistics. OECD Publishing, Paris. DOI: 10.1787/factbook-2010-en.
- [2] OECD (2016) "Municipal waste" in OECD Factbook 2015-2016: Economic, Environmental and Social Statistics. OECD Publishing, Paris. DOI: 10.1787/factbook-2015-en.
- [3] Annual Report on the Environment, the Sound Material-Cycle Society and Biodiversity in Japan 2018. <http://www.env.go.jp/en/wpaper/2018/pdf/07.pdf>, Accessed 1 July 2019
- [4] Kubuki S, Kawakami N, Kamikawa T, Fukagawa M, Nishizumi T, Nishida T, Homonnay Z, Kuzmann E (2005) Corelationship between local structure and water purifying ability of iron-containing waste glasses. *Hyperfine Interact.* 166: 429-436
- [5] Kubuki S, Iwanuma J, Akiyama K, Homonnay Z, Kuzmann E, Nishida T (2013) Water cleaning ability and local structure of iron-containing soda-lime silicate glass. *Hyperfine Interact.* 218:41-45.
- [6] Kubuki S, Iwanuma J, Takahashi Y, Akiyama K, Homonnay Z, Sinkó K,

- 293 Kuzmann E, Nishida T (2014) Visible light-activated catalytic effect of iron-
294 containing soda-lime silicate glass characterized by ^{57}Fe -Mössbauer spectroscopy. J.
295 Radioanal. Nucl. Chem. 301:1–7
- 296 [7] Iida Y, Akiyama K, Kobzi B, Sinkó K, Homonnay Z, Kuzmann E, Ristić M,
297 Krehula S, Nishida T, Kubuki S (2015) Structural analysis and visible light-activated
298 photocatalytic activity of iron-containing soda-lime aluminosilicate glass. J. Alloys
299 Comp. 645:1–6
- 300 [8] Ishikawa S, Kobzi B, Sunakawa K, Nemeth S, Lengyel A, Kuzmann E, Homonnay
301 Z., Nishida T, Kubuki S (2017) Visible-light activated photocatalytic effect of glass
302 and glass-ceramic prepared by recycling waste slag with hematite. Pure Appl. Chem.
303 89(4): 535-544
- 304 [9] Wakasa M, Kobayashi Y, Okano M (2006) Magnetic Field Effect on the
305 Photocatalytic Reaction with TiO_2 Semiconductor Film. Bull. Soc. Sci. Photo. Jpn.
306 69(4) 271-275 (in Japanese)
- 307 [10] Scherrer P (1918) Bestimmung der Größe und der inneren Struktur von
308 Kolloidteilchen mittels Röntgenstrahlen. Göttinger Nachrichten Gesell. 2:98-100
309 (in Germany)
- 310 [11] F. Van der Wurde (1967) Mössbauer effect in $\alpha\text{-Fe}_2\text{O}_3$. Physica Status Solidi (b)
311 17(1): 417- 432
- 312 [12] Murad E, Johnston J. H. (1984) In: Long G. J. (ed) Mössbauer Spectroscopy Applied
313 to Inorganic Chemistry, Vol. 2, Plenum Press, New York, pp. 523-531
- 314 [13] Hirabayashi D, Sakai Y, Yoshikawa T, Mochizuki K, Kojima Y, Suzuki K, Ohshita
315 K, Watanabe Y (2006) Mössbauer characterization of calcium-ferrite oxides
316 prepared by calcining Fe_2O_3 and CaO . Hyperfine Interact. 167(1-3):809-813
- 317 [14] Matsumoto Y, Omae M, Sugiyama K, Sato E. I (1987) New photocathode materials
318 for hydrogen evolution: CaFe_2O_4 and $\text{Sr}_7\text{Fe}_{10}\text{O}_{22}$. J. Phys. Chem. 91(3): 577–581
- 319 [15] Matsumoto Y, Sugiyama K, Sato E. I (1988) Improvement of CaFe_2O_4 photocathode
320 by doping with Na and Mg. J. Solid State Chem. 74(1): 117–125

- 321 [16] Sivula K, Le Formal F, Grätzel M (2011) Solar Water Splitting: Progress Using
322 Hematite (α -Fe₂O₃) Photoelectrodes. *ChemSusChem*, 4: 432–449.
- 323 [17] Iandolo B, Wickman B, Zorić I, Hellman A (2015) The Rise of Hematite: Origin and
324 Strategies to Reduce the High Onset Potential for the Oxygen Evolution Reaction. *J.*
325 *Mater. Chem. A* 3: 16896– 16912.
- 326
- 327
- 328