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Visible light activated photo-catalytic effect and local structure of iron silicate glass prepared by sol-gel method

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Abstract A relationship between methylene blue (MB) decomposition ability under visible light and local structure of $x\mathrm{Fe_2O_3}\cdot(100\text{-}x)\mathrm{SiO_2}$glass abbreviated as xFS prepared by sol-gel method was investigated by ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry (XRD) and ultraviolet-visible light absorption spectroscopy (UV-Vis). Mössbauer spectra of xFS glass with x of 10, 30 and 50 annealed at 1000 °C for 3 h were mainly composed of a paramagnetic doublet due to fayalite ($\mathrm{Fe_2SiO_4}$), and magnetic sextets due to magnetite ($\mathrm{Fe_3O_4}$) or hematite (α-$\mathrm{Fe_2O_3}$). The absorption area (A) of α-$\mathrm{Fe_2O_3}$ gradually increased from 0.0 to 10.3 and 100 % with the increasing $\mathrm{Fe_2O_3}$ content (x) of annealed xFS glass. A leaching test performed by 20 mL of MB aqueous solution and 40 mg of annealed 50FS glass showed that MB concentration decreased from 16.2 to 4.7 μmol $\mathrm{L^{-1}}$ after 2 h with

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the first order rate constant of 1.8×10^{-4} s^{-1}. These results prove that annealed iron silicate glass containing α-Fe_2O_3 can decompose MB effectively under visible light irradiation.

Keywords Iron silicate glass · Sol-gel method · ^{57}Fe-Mössbauer spectroscopy · Photo-catalytic effect · Methylene blue

1 Introduction

Anatase type TiO_2 is well known as a photo-catalyst which is activated by UV light with the wavelength shorter than 380 nm [1]. It will be more effective to develop other photo-catalysts which show their activity under visible light irradiation because anatase type TiO_2 is the only photo catalyst applicable for environmental purification. Many visible light activated photo-catalysts mainly composed of anatase type TiO_2 have been developed [2, 3]. However, only a few examples of visible-light activated photo catalyst *without* anatase type TiO_2were also reported.

Recently, Kubuki et al. reported that iron containing soda-lime silicate glass prepared by recycling the ash discharged from municipal garbage combustion plant was effective to reduce the chemical oxygen demand (COD) of artificial waste water [4, 5]. It showed that iron containing soda-lime silicate glass might be utilized for cleaning polluted waters. In this study, a relationship between local structure and visible light activated photo-catalytic effect of $x$$Fe_2O_3$·(100-$x$)$SiO_2$ glass prepared by sol-gel method was investigated by means of ^{57}Fe-Mössbauer spectroscopy, X-ray diffraction (XRD) and Ultraviolet-Visible absorption spectroscopy (UV-Vis).

2 Experimental

Iron silicate glass with a composition of $x$$Fe_2O_3$·(100-$x$)$SiO_2$ (x = 10–50 in mass%, abbreviated as xFS) was prepared by a sol-gel method. Reagent chemicals of $Si(OC_2H_5)_4$, $Fe(NO_3)_3$·$9H_2O$, 7.8 M HNO_3, and C_2H_5OH were poured into a beaker and mixed well for 2 h at RT. After having been agitated by reflux-heat method at 80 °C for 2 h, the solution was poured into a glass vial and dried at 60 °C for 3 days to prepare dark brown XRD amorphous sample. The prepared glass was annealed at 1000 °C for 3 h in air. ^{57}Fe-Mössbauer spectra were measured by a constant acceleration mode with a source of ^{57}Co(Rh) with α-Fe as a reference. XRD diffraction patterns were recorded at 2θ between 10° and 80° with an intervals and scanning rate of 0.02° and 5°min^{-1}, respectively. X-ray with the wavelength (λ) of 1.54 Å was generated by Cu filament targeted by electrons accelerated by 50 kV voltage at 300 mA current. For evaluation of photo-catalytic effect, 40 mg of well-pulverized annealed xFS glass was soaked into 20 mL of methylene blue aqueous solution (MB_{aq}) with the concentration of 16.2 μM(=5.2 mg L^{-1}). Leaching test was carried out for 2 h at RT using a glass vial irradiated with a visible light having the wavelength range of 420–750 nm. Absorbance of MB_{aq} before and after the irradiation was determined by UV-vis spectrometry within the wavelength of 200 and 800 nm using a source of tungsten-deuterium lamp under the output power of 20 W.

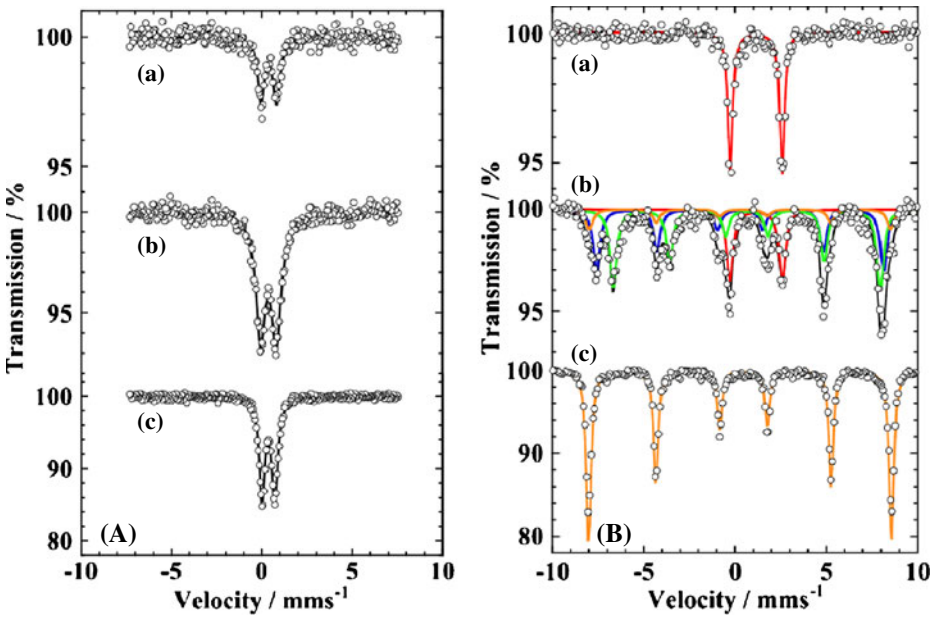

Fig. 1 ^{57}Fe-Mössbauer spectra of xFe$_2$O$_3$·(100–x)SiO$_2$ glass with 'x' of **a** 10, **b** 30 and **c** 50 measured (**A**) before and (**B**) after annealing at 1000 °C for 3 h

3 Results and discussion

^{57}Fe-Mössbauer spectra of xFe$_2$O$_3$·(100–x)SiO$_2$ glass with 'x' of 10, 30 and 50 before and after annealing at 1000 °C for 3 h are shown in Fig. 1. Before the annealing, all the spectra were composed of a paramagnetic doublet with a constant isomer shift (δ) of $0.38_{\pm0.01}$ mm s^{-1} and decreasing quadruplole splitting (Δ) from 0.85 to $0.70_{\pm0.02}$ mm s^{-1} with the increase of 'x' from 10 to 50, indicating that $Fe^{III}O_4$ tetrahedra (T_d) decreased the local distortion with the increase of Fe$_2$O$_3$ content (Fig. 1A (a–c)). On the other hand, Mössbauer spectrum of 10FS glass after isothermal annealing at 1000 °C for 3 h (Fig. 1B (a)) showed a paramagnetic doublet with δ of $1.16_{\pm0.01}$ and Δ of $2.83_{\pm0.02}$ mm s^{-1}, indicating a precipitation of fayalite (Fe$_2$SiO$_4$) [6]. In the case of annealed 30FS glass, the Mössbauer spectrum composed of a doublet and two sextets due to fayalite (δ: $1.16_{\pm0.01}$ mm s^{-1}, Δ: $2.86_{\pm0.02}$ mm s^{-1} and A: $18.0_{\pm0.5}$ %) and magnetite (Fe$_3$O$_4$, δ: $0.28_{\pm0.01}$ mm s^{-1}, H_{int}: $48.9_{\pm0.5}$ T and A: $31.5_{\pm0.5}$ % for tetrahedral (T_d) Fe^{III}, and δ: $0.65_{\pm0.01}$ mm s^{-1}, H_{int}: $45.3_{\pm0.5}$ T and A: $45.3_{\pm0.5}$ % for octahedral (O_h) Fe^{II+III}) (Fig. 1B (b)). Furthermore, only a sextet due to hematite (α-Fe$_2$O$_3$) with δ of $0.37_{\pm0.01}$ mm s^{-1}, and H_{int} of 51.4 $_{\pm0.5}$ T was observed for annealed 50FS glass (Fig. 1B (c)). These results show that the chemical environment of iron in annealed xFS glass varies with the concentration of Fe$_2$O$_3$.

XRD patterns of xFS glass with 'x' of 10, 30 and 50 before and after the annealing were shown in Fig. 2. Several peaks with small intensity and broad linewidth were observed for the XRD patterns of xFS glass before annealing (Fig. 2A (a–c)), indicating that xFS glass had amorphous structure. It should be noted that the halo

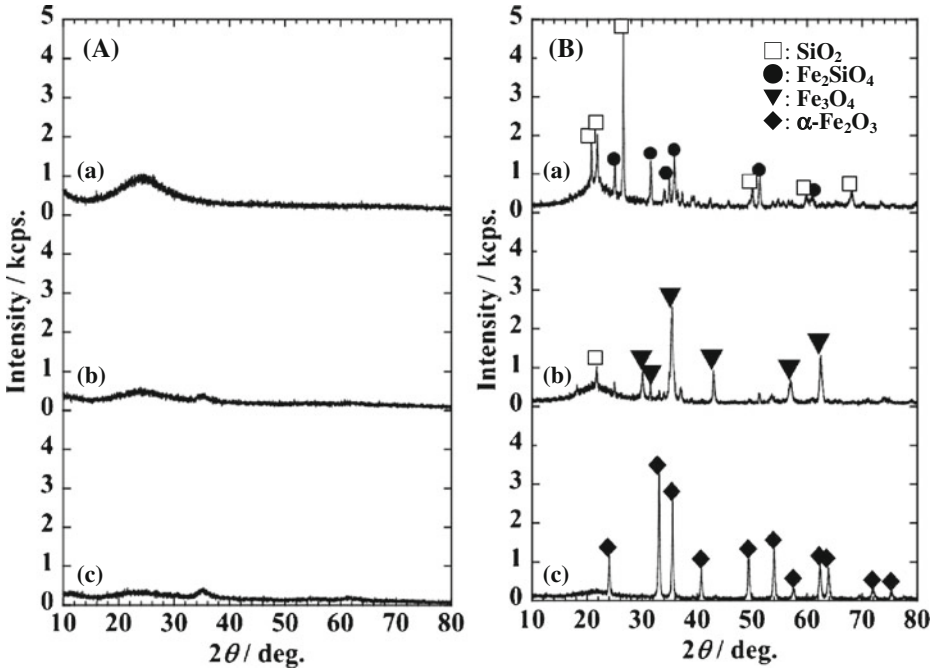

Fig. 2 XRD patterns of xFe$_2$O$_3$·(100–x)SiO$_2$ glass with 'x' of **a** 10, **b** 30 and **c** 50 measured (**A**) before and (**B**) after annealing at 1000 °C for 3 h

XRD pattern was confirmed for xFS glass with 'x' of 50 even though iron is not a typical network former (NWF) like silicon. On the contrary, sharp intense peaks attributed to fayalite (Fe_2SiO_4, PDF No.: 98-000-0049, 2Θ: 25.1°, 31.6°, 35.0°, 35.9°, 51.4°and 60.8°), magnetite (Fe_3O_4, PDF No.: 98-000-0073, 2Θ: 30.1°, 31.6°, 35.4°, 43.0°, 57.0° and 62.5°) and hematite (α-Fe_2O_3, PDF No.: 98-000-0060, 2Θ: 24.0°, 33.1°, 35.5°, 40.8°, 49.4°, 54.0°, 57.4°, 64.3°, 63.9°, 72.0° and 75.3°) could be observed for annealed xFS glass with 'x' of 10, 30 and 50, respectively. There were no peaks attributed to crystalline phases containing carbon were observed. This result shows that the crystalline phases of annealed xFS glass can be controlled by the changing the Fe_2O_3/SiO_2 ratio. It should be noted that there are no peaks attributed to crystalline silicate in the XRD pattern of annealed 50FS glass, implying that α-Fe_2O_3 phase is dispersed in the amorphous glass matrix composed by silicate.

UV-Vis spectra of 20 mL MB_{aq} leached with 40 mg of annealed xFS glass with 'x' of 10, 30 and 50 under visible light irradiation for 2 h were shown in Fig. 3. MB concentration is determined by Lambert-Beer equation, *i.e.*,

$$\log_{10}(I_0/I) = \varepsilon C_t l, \tag{1}$$

where I_0, I, ε, C_t and l are intensity of incident beam, that of transmitting light beam, molar absorption coefficient (=9.5 × 10^4 L mol^{-1} cm^{-1} at 665 nm for MB_{aq} [7], MB concentration after t-min leaching and cell length (=1 cm), respectively. No significant changes of UV-Vis spectra were observed in 2h-leaching test using annealed xFS glass with 'x' of 10 and 30 under visible light irradiation (Fig. 3b–c).

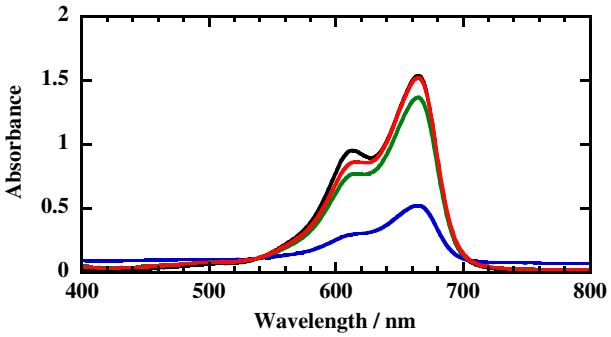

Fig. 3 UV-Vis spectra of MB_{aq} measured before (*black*) and after 2 h visible light irradiation of annealed $x Fe_2O_3 \cdot (100–x) SiO_2$ glass with 'x' of 10 (*red*), 30 (*green*) and 50 (*blue*)

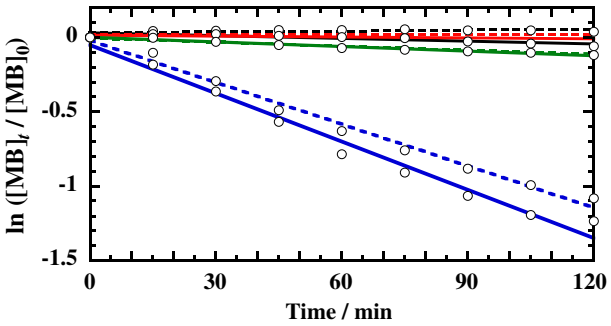

Fig. 4 $\ln[MB]_t/[MB]_0$ *vs. t* plot of leaching test using 20 mL MB_{aq} and 40 mg of annealed $x Fe_2O_3 \cdot (100–x) SiO_2$ glass with 'x' of 10 (*red*), (c) 30 (*green*) and 50 (*blue*) under visible light (*solid line*) and without visible light (*dashed line*). *Black lines* show the leaching test without the glass samples

In contrast, a remarkable decrease in the absorbance of MB from 1.54 to 0.45 was observed for the 2h-leaching test using annealed xFS glass with 'x' of 50 under visible light irradiation (Fig. 3 blue). This result shows that the concentration of MB was decreased from 16.2 to 4.72 μM after 2h-leaching using annealed 50FS glass under visible light irradiation.

Apparent first order rate constant of MB decomposition (k) can be estimated by following equation:

$$\ln (C_t/C_0) = -kt, \tag{2}$$

where C_0 is MB concentration of before leaching (=16.2 μM). By using this equation, k values for MB decomposition caused by annealed xFS with 'x' of 10, 30 and 50 under visible light irradiation were respectively estimated to be 3.65×10^{-6}, 1.56×10^{-5} and 1.80×10^{-4} s^{-1}, as shown in solid lines of Fig. 4. On the other hand, the smaller k's of -2.40×10^{-7}, 1.45×10^{-5} and 1.56×10^{-4} s^{-1} were estimated for the leaching test of the corresponding annealed xFS glass without visible light irradiation, as indicated in dashed lines of Fig. 4. These results prove that annealed xFS glass showed visible light activated photo-catalytic effect when it contains α-Fe_2O_3. Band gap energy (E_g) of Fe_2SiO_4, $Fe_3O_4$and α-Fe_2O_3 was reported to be 7.8 eV [8], 0.1 eV [9, 10] and 2.2 eV [11, 12], respectively. It can be considered that visible light photo-catalytic effect could not be observed for the leaching test using annealed xFS glass with 'x' of 10 and 30 because E_g of the precipitated crystalline phases were not appropriate for the visible light photo catalytic reaction. On the contrary, E_g value of α-Fe_2O_3 (=2.2 eV) precipitated in annealed xFS glass with 'x'

of 50 is suitable for visible light photo catalytic effect because electron can be excited from the valence band to the conduction band by the irradiation of visible light with the wavelength of shorter than 564 nm. It is concluded that we could successfully develop and characterize a visible light photo catalytic material from *ubiquitous* elements of Fe, Si and O. This will contribute for the further developments of visible light activated photo catalyst utilized for self cleaning materials or electrode of solar fuel cells.

4 Summary

A relationship between structure and visible light activated photo catalytic effect of $x\mathrm{Fe_2O_3}\cdot(100\text{-}x)\mathrm{SiO_2}$ (xFS) glass before and after isothermal annealing were investigated by ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry and UV-vis spectroscopy. Isothermal annealing at 1000 °C for 3 h of$x$FS glass with 'x' of 10, 30 and 50 resulted in the precipitation of $\mathrm{Fe_2SiO_4}$, $\mathrm{Fe_3O_4}$ and α-$\mathrm{Fe_2O_3}$, respectively. Leaching test using methylene blue aqueous solution ($\mathrm{MB_{aq}}$) and annealed 50FS glass showed the largest first order rate constant (k) of 1.80×10^{-4} $\mathrm{s^{-1}}$under visible light irradiation. It is concluded that crystalline phase precipitated in xFS glass after annealing can be controlled by changing $\mathrm{Fe_2O_3/SiO_2}$ ratio, and that visible light photo-catalytic effect appears when α-$\mathrm{Fe_2O_3}$ phase was precipitated in xFS glass. This newly developed iron silicate glass can be utilized for environmental purification or electrode of solar fuel cell.

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