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Structural analysis and visible light-activated photocatalytic activity of iron-containing soda lime aluminosilicate glass

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ABSTRACT

A relationship between structure and visible light-activated photocatalytic activity of iron-containing soda lime aluminosilicate ($15Na_2O{\cdot}15CaO{\cdot}40Fe_2O_3{\cdot}xAl_2O_3{\cdot}(30-x)SiO_2$) glass (xNCFAS) was investigated by means of ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry (XRD) and UV–visible light absorption spectroscopy (UV–VIS). The ^{57}Fe-Mössbauer spectrum of 11NCFAS glass measured after heat-treatment at 1000 °C for 100 min was composed of a paramagnetic doublet due to $Fe^{III}(T_d)$ and two magnetic sextets due to regular hematite (α-Fe_2O_3) and hematite with larger internal magnetic field. X-ray diffraction patterns of heat-treated xNCFAS samples resulted in decrease of α-Fe_2O_3 and increase of $Ca_2Fe_{22}O_{33}$ or $CaFe_2O_4$ with alumina content. A quick decrease in methylene blue (MB) concentration from 15.6 to 4.7 μmol L^{-1} was observed in the photocatalytic reaction test with 40 mg of heat-treated 11NCFAS glass under visible light-exposure. The largest first-order rate constant of MB decomposition (k) was estimated to be 9.26×10^{-3} min^{-1}. Tauc's plot yielded a band gap energy (E_g) of 1.88 eV for heat-treated 11NCFAS glass, which is smaller than previously reported E_g of 2.2 eV for α-Fe_2O_3. These results prove that addition of Al_2O_3 into iron-containing soda lime silicate glass is favorable for the preparation of improved visible light-photocatalyst with 'ubiquitous' elements.

1. Introduction

Anatase type of TiO_2 is well known as a photocatalyst which can be only activated by UV light with a wavelength (λ) shorter than 380 nm, due to its high band gap energy (3.2 eV) [1]. The sunlight only contains a few percent of this wavelength. In order to effectively utilize the longer wavelength components of the solar spectrum, visible light-activated photocatalysts are investigated. For example doping the TiO_2 structure with different anionic species such as N and transition metal cations Si, Fe, V, Cr [2,3]. Abbrus et al. reported that 1.0 g L^{-1} of Fe^{III}-doped TiO_2 decomposed 0.1 mM phenol with the constant rate of 2.07×10^{-9} s^{-1} under visible light irradiation [4].

Visible light activated photocatalyst can be prepared from other semiconductor materials as well, with more favorable optical band gap. Hematite (α-Fe_2O_3) is a suitable material, due to its photocatalytic properties, chemical stability, nontoxicity and natural availability for applications in water splitting and waste-water treatment [5–7]. Different preparation methods were applied in order to optimize the photocatalytic effect. Chen et al. prepared different hematite crystals with nano-particle, nanotube-, and nanorod-like morphologies. MB degradation experiments showed the best 6.4×10^{-3} min^{-1} rate constant for nano-particles [8]. Cai et al. investigated visible-light photocatalytic activity of mesocrystalline hematite nano plates toward rhodamine B (RhB) [9]. The high surface area resulted in a high rate constant of 2.21×10^{-2} min^{-1} [9]. RhB degradation depending on the surface area of α-Fe_2O_3 similar nanostructures was also evaluated by Liang et al. [10]. The rate constant was estimated to be 5.46×10^{-3} min^{-1} for the nano structured α-Fe_2O_3 with the largest surface area [10]. Iron containing materials also can be made with photocatalytic activity, it was reported that $Zn_{1-x}Fe_xO$ [11], Fe–Cu/TiO_2 [12], Fe–WO_3 [7] and Fe–$BiVO_4$ [13] showed remarkable photocatalytic activity under visible light exposure. These results indicate that Fe plays an important role for visible light-activated photocatalysis.

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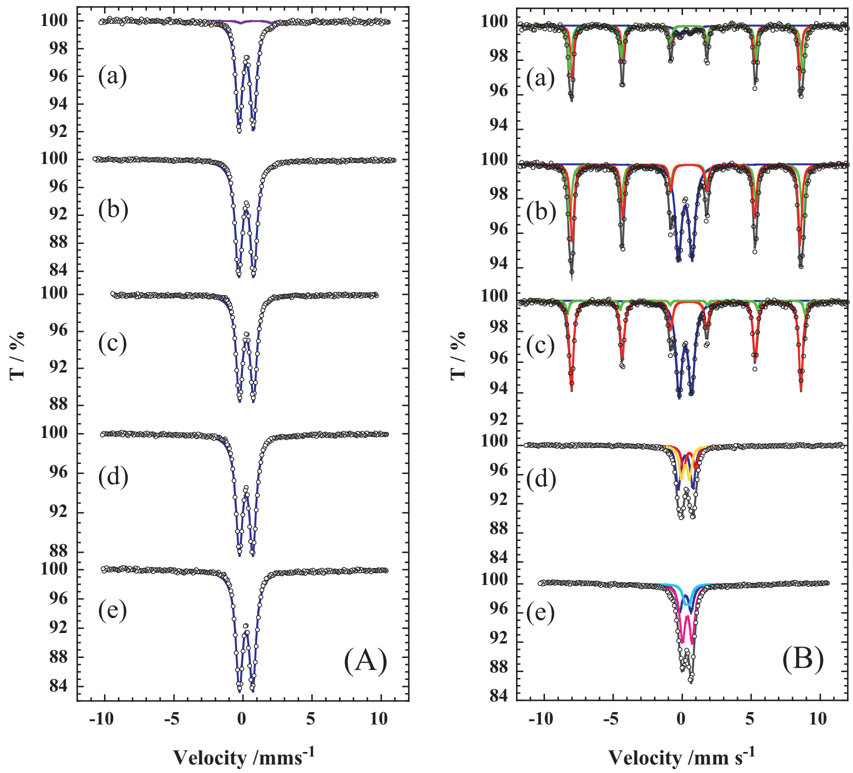

Fig. 1. ^{57}Fe-Mössbauer spectra of $15Na_2O{\cdot}15CaO{\cdot}40Fe_2O_3{\cdot}xAl_2O_3{\cdot}(30-x)SiO_2$ samples with 'x' of (a) 0, (b) 5, (c) 10, (d) 15 and (e) 20; those measured before (A) and after (B) heat-treatment at 1000 °C for 100 min.

Table 1
^{57}Fe-Mössbauer spectra of $15Na_2O{\cdot}15CaO{\cdot}40Fe_2O_3{\cdot}xAl_2O_3{\cdot}(30-x)SiO_2$ samples with 'x' of 0, 5, 10, 15 and 20.; those measured before (left side) and after (right side) heat-treatment at 1000 °C for 100 min.

Sample	Before heat-treatment				Sample	After heat-treatment			
x	Species	A (%)	δ (mm s^{-1})	Δ (mm s^{-1})	Species	A (%)	δ (mm s^{-1})	Δ (mm s^{-1})	H_{int} (T)
0	$Fe^{III}(T_d)$	97.9	0.24	1.04	$Fe^{III}(T_d)$	8.1	0.23	0.84	–
	$Fe^{II}(T_d)$	2.1	0.95	2.21	$Fe^{3+}(O_h)$mag.	44.8	0.39	−0.20	51.2
					$Fe^{3+}(O_h)$mag.	47.1	0.39	−0.20	52.4
5	$Fe^{III}(T_d)$	100	0.23	1.09	$Fe^{III}(T_d)$	35.6	0.23	0.99	–
					$Fe^{3+}(O_h)$mag.	36.0	0.38	−0.18	51.2
					$Fe^{3+}(O_h)$mag.	28.4	0.39	−0.18	52.5
10	$Fe^{III}(T_d)$	100	0.26	1.02	$Fe^{III}(T_d)$	41.3	0.23	0.90	–
					$Fe^{3+}(O_h)$mag.	53.0	0.38	−0.18	51.6
					$Fe^{3+}(O_h)$mag.	5.7	0.39	−0.19	53.4
15	$Fe^{III}(T_d)$	100	0.22	0.98	$Fe^{III}(T_d)$	43.9	0.20	0.88	–
					$Fe^{III}(O_h)$	23.7	0.44	0.73	–
					$Fe^{III}(O_h)$	32.4	0.19	0.49	–
20	$Fe^{III}(T_d)$	100	0.21	0.97	$Fe^{III}(T_d)$	27.6	0.23	0.84	–
					$Fe^{III}(O_h)$	56.8	0.37	0.70	–
					$Fe^{III}(O_h)$	15.7	0.37	0.31	–

A: absorption area, δ: isomer shift, Δ: quadrupole splitting, H_{int}: internal magnetic field.

Precipitation of α-Fe_2O_3 was confirmed from the ^{57}Fe-Mössbauer spectrum of $15Na_2O{\cdot}15CaO{\cdot}50Fe_2O_3{\cdot}20SiO_2$ glass heat treated at 1000 °C for 100 min, and a high rate constant (k) of 2.87×10^{-2} h^{-1} for methylene blue (MB) decomposition was estimated on the basis of the photocatalytic reaction test using heat-treated glass under visible light-irradiation [14]. This result indicated that heat-treated soda lime iron silicate glass shows visible light-activated catalysis due to the presence of α-Fe_2O_3. And the largest absorption area of α-Fe_2O_3 was confirmed from the ^{57}Fe-Mössbauer spectrum (93.1%) of $15Na_2O{\cdot}15CaO{\cdot}40Fe_2O_3{\cdot}20SiO_2$ glass heat treated at 1000 °C for 100 min [14].

Aluminate glass is known as infrared (IR) light-transmitting material having wider optical transparency ranging from visible to infrared region [15]. Due to the high IR light-transmittance