



Synergistic effect of different phase on the photocatalytic activity of visible light sensitive silver antimonates

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ABSTRACT

We investigated phase transition of ilmenite-type AgSbO_3 to pyrochlore by post-heat treatment and the synergy effect of the mixed phases of AgSbO_3 on the photocatalytic activities to enhance the activities. The AgSbO_3 with an ilmenite structure was prepared by a cation-exchange method. Phase transition from the ilmenite to pyrochlore occurred by proper control of post-heat treatment. The sample that was obtained by post-heat treatment of ilmenite-type AgSbO_3 at 660°C for 3 h consisted of both of the ilmenite and pyrochlore phases, and the sample at 685°C for 4 h mainly consisted of the pyrochlore phase. Together with an increase in the ratio of the pyrochlore phase, the optical absorption spectra blue-shifted. The band gaps of single phases of the ilmenite and the pyrochlore were 2.4 and 2.6 eV, respectively. The AgSbO_3 sample obtained by post-heat treatment at 660°C for 3 h showed about eight times and twice higher photocatalytic activity under visible light irradiation than a standard TiO_2 photocatalyst (Degussa P25) and single phase of the ilmenite-type sample, respectively, because of the synergy effect.

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1. Introduction

Titanium-dioxide (TiO_2) photocatalyst is utilized for many application fields, such as self-cleaning materials and air cleaners [1,2] because this oxide shows high photocatalytic activity under UV (ultraviolet) light irradiation. Most of commercially available TiO_2 is rutile- or anatase-type one. As for photocatalytic activity, anatase-type TiO_2 is usually superior to rutile one. Moreover, TiO_2 with the mixed phases (rutile and anatase) is often reported to show higher activity than each of the single phases of TiO_2 because of the synergistic effect, which leads to enhancement of charges (photogenerated electrons and holes) separation and an increase in the lifetime of the charges [3–5].

For indoor application development of visible light sensitive photocatalysts has been intensively studied because visible light ($400\text{ nm} < \lambda < 800\text{ nm}$) is a main component in indoor illumination. Titanium dioxide that is doped with a foreign metal ion or a non-metal ion is a promising visible light sensitive photocatalyst [6–12]. Except for these photocatalysts, some complex metal oxides are also promising [13–19]. Especially, Ag-containing complex oxides including AgNbO_3 are candidates of visible light sensitive photo-

catalysts [17], and doping of a silver ion often narrows the band gap [18].

Apart from AgNbO_3 , two types of AgSbO_3 (pyrochlore and ilmenite phases) are also known as visible light sensitive photocatalysts [20,21]. The ilmenite phase is a metastable phase, which transforms into a more stable pyrochlore phase by heat treatment in a suitable condition. So, AgSbO_3 consisting of the two phases might be prepared by proper control of heating conditions. Since the synergistic effect leads to higher activity on the mixed phases of anatase and rutile TiO_2 [3,4], we considered that the mixed phases of the ilmenite- and pyrochlore-type AgSbO_3 might be a promising visible light sensitive photocatalyst. Moreover, to the best of our knowledge, there are very few researches about the synergistic effect on the activity of visible light sensitive photocatalysts. Thus, in this study, we selected AgSbO_3 as a candidate of a visible light sensitive photocatalyst, and investigated the relationship between the activity and the ratio of the ilmenite phase in the mixed phase AgSbO_3 for development of the photocatalyst with higher activity and for researches about the synergistic effect on the activity. The ratio of the ilmenite phase was mainly controlled by post-heating temperature.

2. Experimental

2.1. Sample preparation

For preparation of AgSbO_3 with an ilmenite phase, first of all, NaSbO_3 powder was prepared by a solid-state-reaction method.

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The stoichiometric amount of Sb_2O_5 (Kojundo Chem. Co., Japan) and 5% excess of Na_2CO_3 (Junsei Chem. Co., Japan) were mixed on a mortar, and the mixture was calcined at 900°C for 8 h. The calcined powder was washed over and over again with distilled water and dried at 120°C for 5 h. Then NaSbO_3 was obtained. Powder of AgSbO_3 with an ilmenite phase was prepared by a cation-exchange method [22,23], and AgNO_3 , KNO_3 , and NaSbO_3 were utilized as starting materials. These compounds (AgNO_3 , KNO_3 , and NaSbO_3) were mixed with a molar ratio of 1:1.03:1 on a mortar, and the mixture was heated at 210°C for 36 h in air [24,25]. The obtained powder was washed with distilled water over and over again to remove remaining nitrates and dried at 120°C for 5 h. Then, we obtained AgSbO_3 with an ilmenite phase. Addition of KNO_3 promotes ion exchange from Na^+ to Ag^+ and suppresses decomposition of AgNO_3 [22].

Ilmenite-type AgSbO_3 is a metastable compound. By post-heating it at around $600\text{--}800^\circ\text{C}$, phase transition of AgSbO_3 from the ilmenite phase to a pyrochlore phase occurs [23]. For investigation of the effect of the phase transition on the photophysical and photocatalytic properties, the ilmenite-type AgSbO_3 samples were post-heated at several kinds of temperatures (650 , 655 , 660 , 670 , and 685°C) for 4 h, respectively. As a result, five AgSbO_3 samples consisting of both phases were able to be prepared. As a reference, a mechanically mixed AgSbO_3 sample consisting of both phases was also prepared. The as-prepared sample (ilmenite) and the sample obtained by post-heat treatment at 685°C for 4 h were mixed with a mixing ratio of 1:1 on a mortar for 30 min. Then, we obtained a mechanically mixed sample.

2.2. Characterization

The crystal structures and phase impurity of the prepared samples were determined with an X-ray diffractometer (XRD, JDX-3500; JEOL, Japan) with $\text{Cu K}\alpha$ radiation. The relative amount of the pyrochlore phase in the post-heated sample was determined from the X-ray diffraction (XRD) patterns using the following equation [26,27]:

$$\text{ratio of pyrochlore} = \frac{I_{\text{pyro}}}{I_{\text{pyro}} + I_{\text{ilm}}}, \quad (1)$$

where I_{pyro} and I_{ilm} are the intensities of the major X-ray peak ($2\theta = 30.2^\circ$) for the pyrochlore phase and the $(1\ 1\ 0)$ peak ($2\theta = 33.6^\circ$) for the ilmenite phase, respectively. The ratio of Na to Sb was evaluated with an energy dispersive X-ray spectrometer (EDS, EX-230; JEOL).

The diffuse reflectance spectra were measured with a UV-vis spectrophotometer (UV-2500PC; Shimadzu Co., Japan) using BaSO_4 powder as a reference. The spectra were transformed to absorption spectra using the Kubelka–Munk relationship. The specific surface area was evaluated with a surface-area analyzer (Gemini 2360; Micromeritics Corp., USA) by a BET (Brunauer–Emmett–Teller) method at 77 K. The surface areas of the as-prepared sample and the samples post-heated at 650 , 655 , 660 , 670 , and 685°C were 3.3 , 2.5 , 2.3 , 2.8 , 2.8 , and $2.6\ \text{m}^2\ \text{g}^{-1}$, respectively.

Evaluation for photocatalytic activity was performed in a cylindrical glass reactor in 500 ml of volume at room temperature. Photocatalytic decomposition of gaseous acetaldehyde into CO_2 under visible light irradiation was selected as a model of reaction. The detailed evaluation method was described as follows. Powder of 0.4 g of the photocatalyst was spread uniformly over $8.5\ \text{cm}^2$ of the area in the center of the base of the reactor. The inside atmosphere was replaced with dry air, and then the mixed gases comprising dry air and acetaldehyde were introduced. By this operation, the acetaldehyde concentration in the reactor became about 400 ppm. The reactor was kept in the dark till the adsorption–desorption–equilibrium state was established. Then

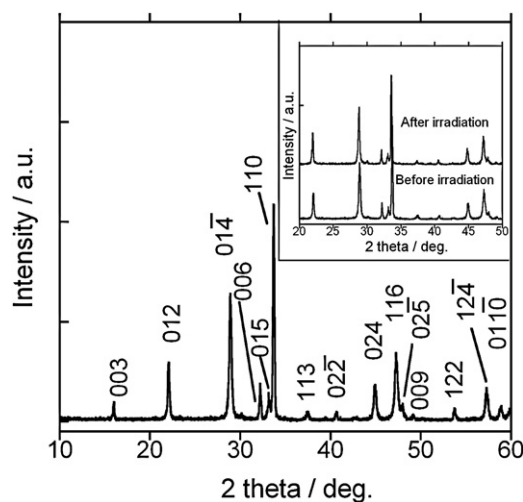


Fig. 1. XRD pattern of the as prepared AgSbO_3 . The inset is the XRD patterns of the AgSbO_3 before and after 12 h of visible light ($\lambda > 400\ \text{nm}$) irradiation.

visible light ($400\ \text{nm} < \lambda < 530\ \text{nm}$) irradiation was performed using 300 W of a Xe lamp, water filter, and several types of glass filters (Y-44, HA-30 and B390, Hoya Corp., Japan). The concentrations of acetaldehyde and CO_2 were measured using a gas chromatograph (GC-14B; Shimadzu) with a flame-ionization detector (FID) and a methanizer. The intensity of the light irradiation for the photocatalytic activity evaluation was measured with a spectroradiometer (USR-40D; Ushio Corp., Japan) and adjusted to $0.9\ \text{mW}\ \text{cm}^{-2}$.

2.3. Calculation of band structures

The plane-wave density functional theory (DFT) was applied to calculate the band structures and the density of states (DOS) of AgSbO_3 using the program of Cambridge serial total energy package (CASTEP) [28,29]. The core electrons were replaced with ultra-soft pseudo potentials, and the interactions of exchange and correlation were treated within the framework of the generalized gradient approximation (GGA). The k space integration for the ilmenite-type AgSbO_3 was done in the Brillouin zone of six unit cells ($[\text{AgSbO}_3]_6$), and the integration for the pyrochlore was done in the zone of 16 unit cells ($[\text{AgSbO}_3]_{16}$). The k -points were generated by the Monkhorst–Pack scheme [30]. The kinetic energy cutoff was selected as 380 eV for calculations of the ilmenite-type and the pyrochlore-type AgSbO_3 .

3. Results and discussion

3.1. Crystal structure

Prior to preparation of the ilmenite-type AgSbO_3 , NaSbO_3 was prepared. When stoichiometric amounts of Na_2CO_3 and Sb_2O_5 were mixed and calcined, the obtained powder mainly consisted of ilmenite-type NaSbO_3 , but Sb_2O_5 still remained as an impure phase. This is because the Na ion was partially volatilized during calcination [31]. So, by addition of 5% excess of Na_2CO_3 , we succeeded in preparation of NaSbO_3 with a single phase. The ratio of Na to Sb on this NaSbO_3 was confirmed to be 1 with an EDS. By using this NaSbO_3 and AgNO_3 , AgSbO_3 was prepared. The phase impurity and crystal structures of the prepared AgSbO_3 were evaluated with XRD, as shown in Fig. 1. Judging from the previous report [23], we considered that the sample was basically formed in a single phase of ilmenite-type AgSbO_3 with a space group of $R\bar{3}$.

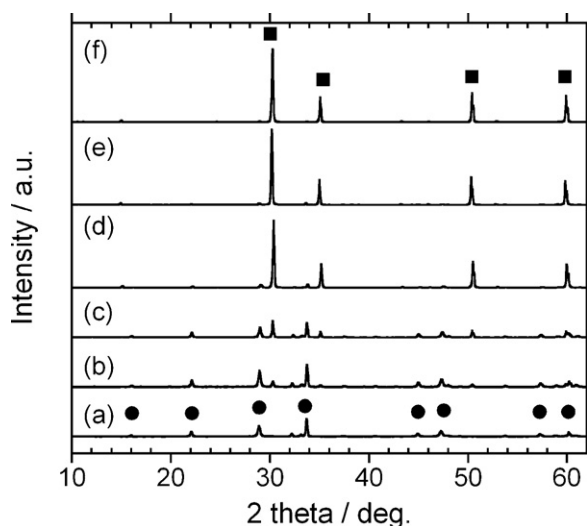


Fig. 2. Relationship between the XRD patterns of the post-heated samples and post-heating temperatures: (a) as prepared sample, (b) sample post-heated at 650 °C for 4 h, (c) sample at 655 °C, (d) sample at 660 °C, (e) sample at 670 °C, and (f) sample at 685 °C.

The ilmenite phase of AgSbO_3 is metastable. So, the phase transforms into the more stable pyrochlore phase by post-heating at proper temperature. Fig. 2 shows change in the XRD patterns of the post-heated samples. The pyrochlore phase first appeared at 650 °C, and weak peaks from the ilmenite phase were still observed after heat treatment at 685 °C. Also, we found that with an increase in the heating temperature the intensity of the XRD peaks belonged to the pattern of the ilmenite phase gradually decreased but those belonged to the pyrochlore-phase pattern increased. These results suggested that the amount of the pyrochlore phase increased but the amount of the ilmenite phase decreased in the sample with the heating temperature. To qualitatively estimate the relative ratio of the pyrochlore in the sample, we calculated the ratio using the above mentioned equation (1). The relationship between the post-heating temperature and the ratio of pyrochlore is shown in Fig. 3. It is clearly seen that phase transition drastically promoted at the temperatures between 650 and 660 °C. And the sample at 685 °C was found to mainly consist of the pyrochlore phase. Detailed phase-transition mechanism of AgSbO_3 is still unclear, but the mechanism of the other photocatalyst including TiO_2 was already reported. In TiO_2 , by proper heat treatment metastable anatase-type TiO_2 phase-transforms into stable rutile-type TiO_2 , and at an initial phase-transition stage small amounts of rutile domains

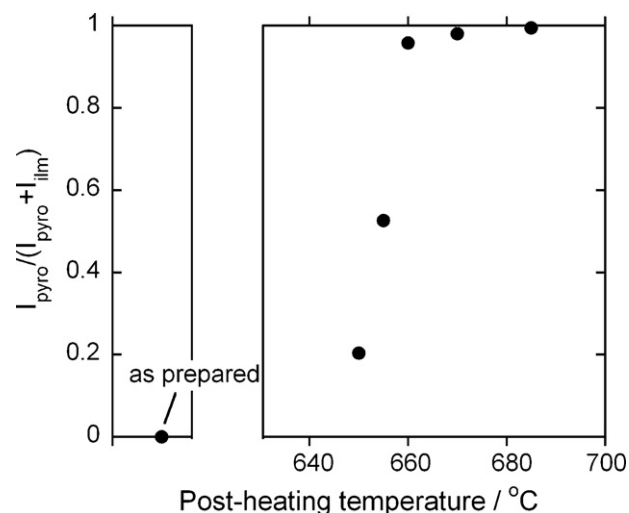


Fig. 3. Post-heating-temperature dependence of change in the ratio of the pyrochlore phase ($I_{\text{pyro}}/(I_{\text{pyro}} + I_{\text{ilm}})$).

are reported to form on the anatase particles [32,33]. The phase-transition mechanism of TiO_2 should be similar to that of AgSbO_3 . So, we consider that the mixed phases of the AgSbO_3 such as the samples at 650 °C for 4 h mainly consisted of ilmenite particles with pyrochlore domains.

3.2. Band calculation

For well understanding of the photophysical and photocatalytic properties on the prepared AgSbO_3 samples, investigation of their electronic band structures is important. The structures of AgSbO_3 were calculated by the plane-wave-based density functional method [28,29]. Figs. 4 and 5 show the band structures and total DOS of the bulk ilmenite- and pyrochlore-type AgSbO_3 , respectively. In the ilmenite, the highest occupied band corresponding to the broad VB is composed of the orbitals that are hybridized with the Ag 4d and the O 2p. This hybridization leads to an increase in the energy at the top of the VB, resulting in a narrower band gap. The bottom of the CB in the ilmenite consists of the Ag 5s, Ag 5p, Sb 5s, O 2s, and O 2p orbitals (see Fig. 4b). The composition of top of the VB and bottom of the CB in the pyrochlore was similar to that in the ilmenite.

The bottom of the CB and the top of the VB in the ilmenite located at the G point and near the A point, respectively, and the bottom of the CB and top of the VB in the pyrochlore located at the G point

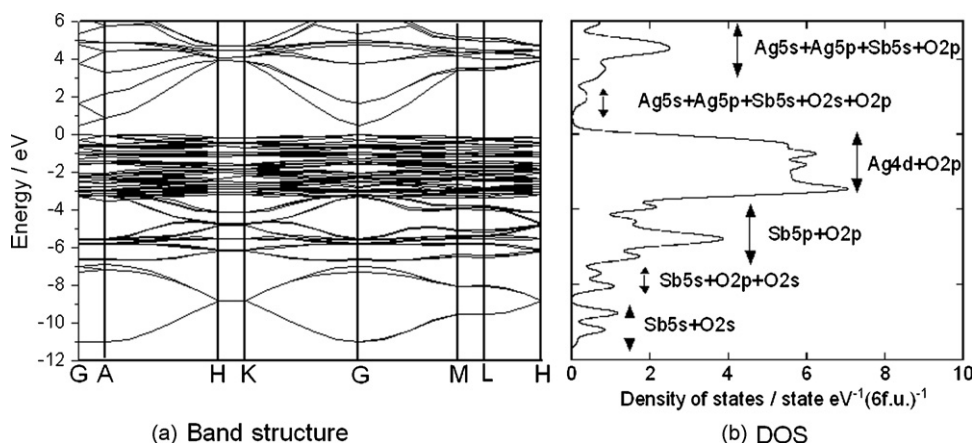


Fig. 4. (a) Calculated band structure of the ilmenite-type AgSbO_3 . (b) Total DOS of the ilmenite-type AgSbO_3 .

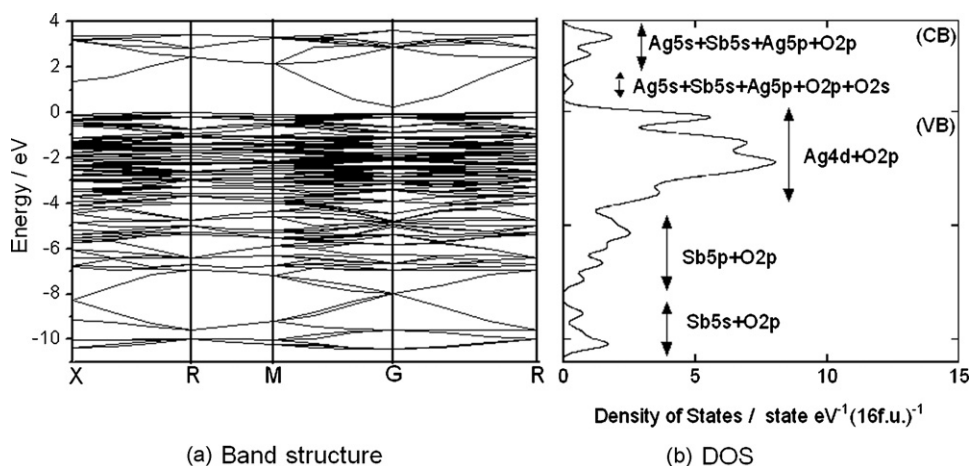


Fig. 5. (a) Calculated band structure of the pyrochlore-type AgSbO_3 . (b) Total DOS of the pyrochlore-type AgSbO_3 .

and at the R point, respectively. Thus, both of the AgSbO_3 should be indirect transition-type semiconductors.

In both AgSbO_3 , the CB near the bottom around the G point shows a large dispersion, suggesting that photogenerated electrons have small effective mass and high mobility. However, the dispersion of the VB near the top suggested that the photogenerated holes should have large effective mass and low mobility.

3.3. Optical absorption spectra

Fig. 6 shows the optical absorption spectra of AgSbO_3 . The as-prepared ilmenite-type sample was yellow and absorbed visible light up to 520 nm. However, this optical absorption spectrum is different from the result, which was previously reported by Singh and Uma [20(a)]. Their prepared sample was yellowish green and had strong absorption from 200 to 1000 nm, suggesting that a large amount of oxygen defects or impurities were formed in their sample [20(a),21].

For qualitative evaluation of the absorption property of AgSbO_3 , its band gap was estimated using the Tauc plot [34]. According to the approach by Tauc et al., the band gap of an indirect transition-type semiconductor can be estimated using the following equation:

$$\alpha h\nu = A(h\nu - E_g)^2, \quad (2)$$

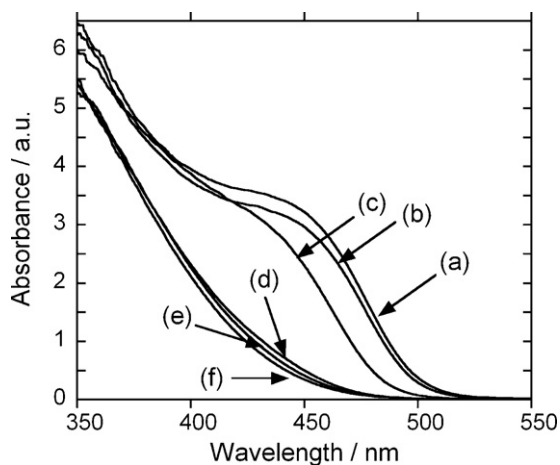


Fig. 6. Optical absorption spectra of the prepared AgSbO_3 : (a) as prepared sample, (b) sample post-heated at 650 °C for 4 h, (c) sample at 655 °C, (d) sample at 660 °C, (e) sample at 670 °C, and (f) sample at 685 °C.

where α is absorption coefficient near the absorption edge, $h\nu$ is the energy of incident photons, and A is constant [34–37]. The band gap of the ilmenite phase was estimated to be 2.4 eV and is smaller than that of the pyrochlore phase (2.6 eV) [21].

From the band gaps and the calculated band structures, we investigated the relative positions of the top of the VB and the bottom of the CB on the ilmenite and pyrochlore phases. As we mentioned above, the composition of top of the VB and bottom of the CB in the ilmenite phase was similar to that in the pyrochlore phase, where the top of the VB and the bottom of the CB mainly consist of the orbitals hybridized with O 2p and some Ag orbitals. The interaction between Ag and O in the ilmenite phase should be stronger than that in the pyrochlore phase because the bond length between Ag and O in the ilmenite phase is shorter than that in the pyrochlore phase [23,38]. So, the energy of the bottom of the CB in the ilmenite phase should be less positive than that in the pyrochlore phase, and the energy of the top of the VB in the ilmenite phase should be less negative than that in the pyrochlore phase.

By post-heating the samples, the crystal structures changed (Fig. 2). Together with the change in their crystal structures, the optical absorption spectra also changed (Fig. 6). Especially, the absorption spectra between the sample post-heated at 650 °C and that at 660 °C drastically changed. The sample at 685 °C mainly consisting of the pyrochlore phase absorbed visible light up to 480 nm, and its optical absorption spectrum was similar to the spectrum of the pyrochlore-type AgSbO_3 [21]. By the phase transition from ilmenite to pyrochlore, the absorption spectrum blue-shifted by about 40 nm.

3.4. Photocatalytic activity

The prepared AgSbO_3 absorbed visible light, and these oxides were possibly promising visible light sensitive photocatalysts. So, evaluation of photocatalytic activity was carried out under visible light irradiation. Decomposition of acetaldehyde was selected as a probe reaction. This is because acetaldehyde is a major indoor volatile organic compound (VOC) and often cause sick building syndrome (SBS) [39–41]. Fig. 7 shows irradiation-time dependence of change in the concentrations of acetaldehyde and a final product, CO_2 over the as-prepared ilmenite-type AgSbO_3 . By light irradiation acetaldehyde concentration decreased and CO_2 concentration increased. This result indicated that acetaldehyde was photocatalytically decomposed into CO_2 over this AgSbO_3 under visible light irradiation. Especially, at the initial stage the CO_2 -evolution concentration was proportional to light-irradiation time,

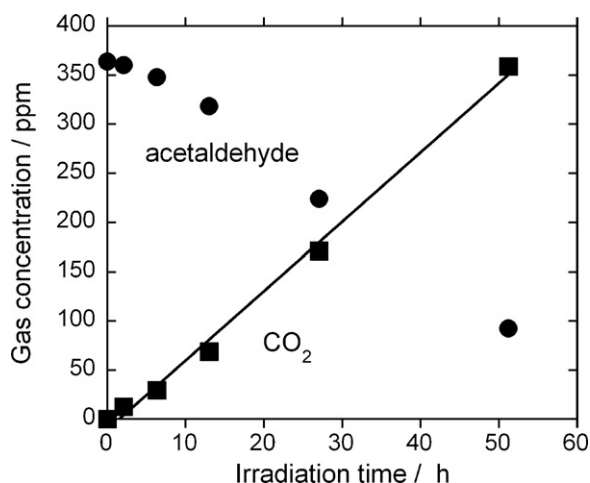


Fig. 7. Irradiation-time dependence of change in the concentrations of acetaldehyde and CO_2 : closed circle, concentration of acetaldehyde; closed square, CO_2 concentration.

indicating that the CO_2 evolution followed pseudo zero-order kinetics.

Also, we confirmed that the CO_2 evolution followed pseudo zero-order kinetics over the post-heated AgSbO_3 . So, their photocatalytic activities were qualitatively compared using the zero-order-reaction rates. Fig. 8 shows the relationship between the post-heating temperatures and the rates for the CO_2 evolution. We found that the photocatalytic activities were largely influenced by slight change in the post-heated temperature. The sample obtained by post-heat treatment of ilmenite-type AgSbO_3 at 650°C for 4 h had a low pyrochlore ratio and the activity of the sample was almost as same as that of the as prepared sample. The samples at 685°C largely consisting of the pyrochlore phase showed much lower activity than the as-prepared sample because the activity of the pyrochlore type AgSbO_3 was reported to be inferior to that of ilmenite-type AgSbO_3 [20]. However, the samples at 655 and 660°C for 4 h with proper pyrochlore ratios showed higher photocatalytic activities than the as-prepared sample. Especially, the sample at 655°C for 4 h showed the highest photocatalytic activity among them, though its surface area was

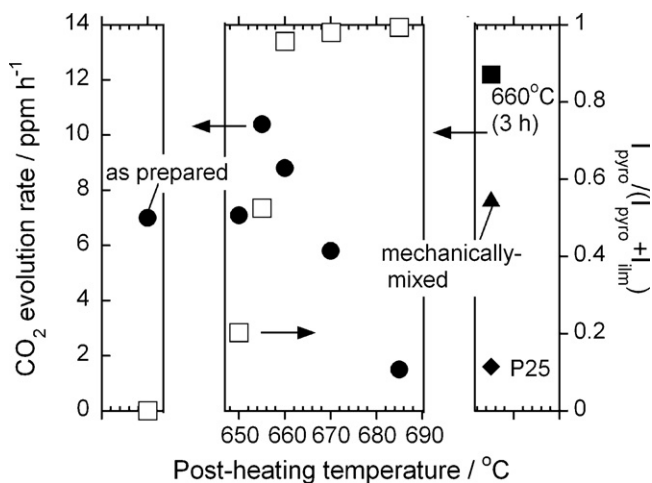


Fig. 8. Post-heating-temperature dependence of change in the CO_2 evolution rates and the ratio of the pyrochlore phase ($I_{\text{pyro}}/(I_{\text{pyro}} + I_{\text{ilm}})$). Closed circle, CO_2 evolution rates over the sample post-heated for 4 h and the as prepared sample; closed square, CO_2 evolution rate over the sample post-heated at 660°C for 3 h; closed rhombus, CO_2 evolution rate over P25; closed triangle, CO_2 evolution rate over mechanically mixed AgSbO_3 ; open square ($I_{\text{pyro}}/(I_{\text{pyro}} + I_{\text{ilm}})$).

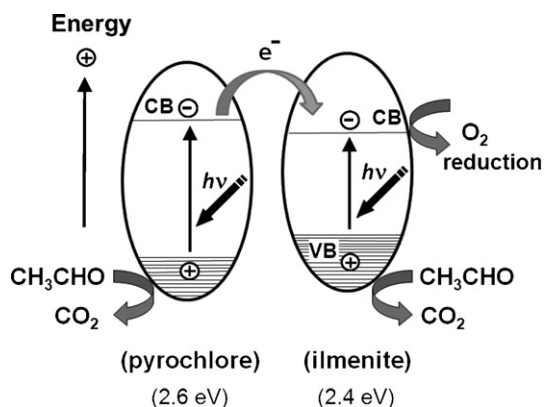


Fig. 9. Proposed model of charge separation on the mixed phase AgSbO_3 .

smallest. Improvement in the crystallinity of the samples by post-heat treatment should not be a dominant reason why the sample at 655°C showed the highest activity because the activity of the sample at 650°C with lower crystallinity was much higher activity than that at 685°C . Rather, phase transition should largely affect the activity. This phase transition was induced by heat treatment, but light-induced phase transition also might occur. So, to check the possibility of light-induced phase-transition, we measured the XRD patterns before and after 12 h of visible light ($\lambda > 400 \text{ nm}$) irradiation. However, we cannot find difference between the patterns (see inset of Fig. 1). From these results, we consider that this material was relatively photo-stable [17,20,24] and phase transition from ilmenite to pyrochlore did not occur by light irradiation.

To understand the differences in the activities of the samples, it is important to discuss the mechanism of the photocatalytic reaction. The proposed mechanism of the photocatalysis with the mixed phase AgSbO_3 is shown in Fig. 9, judging from the band structures of the samples and the previous reports of the hetero-junction semiconductors, such as $\text{Co}_3\text{O}_4/\text{BiVO}_4$ [42,43]. By the visible light irradiation electrons on the VB of the pyrochlore and ilmenite phases were excited to the CB, and the charges (electrons and holes) were generated on the CB and the VB, respectively. The electrons should transfer from the CB in the pyrochlore phase to the CB in the ilmenite phase. This is because the energy at the bottom of the CB in the ilmenite phase should be less positive than that in the pyrochlore phase, as we described in Section 3.3. The holes in the VB of the pyrochlore phase had large effective mass and were difficult to migrate to the VB in the ilmenite phase [44,45]. Rather, the holes in the pyrochlore phase should react with adsorbed acetaldehyde on its own surface. So, charge separation was promoted in the pyrochlore phase. Thus, in case of the sample with a proper amount of the pyrochlore phase, such as the sample at 655°C for 4 h, because of the synergy effect the electron transfer and charge separation were promoted, leading to the enhancement of the activity. However, in case of the sample with a less or excess amount of the pyrochlore phase, the electron transfer was little promoted because of imbalance between the amount of the pyrochlore phase and that of the ilmenite phase, resulting in a lower activity.

In addition, we also controlled post-heating time to prepare the sample with higher activity. Shorter post-heating time made phase transition slightly suppressed and the ratio of the pyrochlore phase decreased. When the as-prepared sample was post-heated at 660°C for 3 h, the pyrochlore ratio of the prepared sample was estimated to be 0.87 ($I_{\text{pyro}}/(I_{\text{pyro}} + I_{\text{ilm}}) = 0.87$). This value was smaller than the ratio of the sample at 660°C for 4 h. As a result, the sample at 660°C for 3 h showed about twice higher activity than ilmenite-

type AgSbO_3 and the highest activity among the prepared samples in this study (Fig. 8). Moreover, the activity of this photocatalyst was estimated to be about eight times higher than that of a commercially available standard TiO_2 photocatalyst (Degussa P25) with relatively higher activity [5]. These results suggested that more proper post-heating conditions (time and temperature) should lead to development of AgSbO_3 with much higher activity.

As a reference, a mechanically mixed sample was also prepared using the as-prepared sample (ilmenite) and the sample (mainly pyrochlore) obtained by post-heat treatment of the as-prepared sample at 685°C for 4 h. The pyrochlore ratio of this mechanically mixed sample was 0.76 and between that of the sample at 655°C for 4 h and that at 660°C for 3 h. Judging from the relationship between the ratios and the photocatalytic activities (see Fig. 8), it was expected that the mechanically mixed sample may show higher activity than the sample at 655°C for 4 h. However, actually, the mechanically mixed sample showed lower activity than the sample at 655°C and slightly higher activity than the as-prepared sample. These results suggested that on the mechanically mixed sample pyrochlore phases interacted with ilmenite phases in the photocatalysis, but this interaction should be weaker than that of the sample at 655°C . Thus, we consider that close interaction between pyrochlore phases and ilmenite phases is necessary for enhancement of photocatalytic activities over the AgSbO_3 samples with the mixed phases.

4. Conclusion

We investigated phase transition of ilmenite structured AgSbO_3 to pyrochlore by post-heat treatment and the synergy effect of the mixed phases of AgSbO_3 on the photocatalytic activities. By post-heating of the ilmenite-type AgSbO_3 under the proper heating conditions, phase transition from ilmenite to pyrochlore occurred. From calculation of the band structure, we found that on ilmenite- and pyrochlore-type AgSbO_3 , photogenerated electrons had high mobility, but the photogenerated holes had low mobility.

The photocatalytic activity was evaluated from decomposition of a harmful gas, acetaldehyde into CO_2 under visible light irradiation. We found that the photocatalytic activities were largely influenced by slight change in the post-heated temperature. The mixed phase- AgSbO_3 sample obtained by post-heat treatment at 660°C for 3 h showed higher photocatalytic activity than single phase of the ilmenite-type sample. Also, the post-heated AgSbO_3 showed about eight times higher photocatalytic activity than a standard TiO_2 , P25. The reason why the sample at 660°C for 3 h showed higher activity may be relevant to promotion of charge separation because of the synergy effect.

By only post-heating of AgSbO_3 under proper conditions (time and temperature) the activity easily improved. Also, we found that development of a mixed phase sample is a useful method for enhancement of the activity even in case of a visible light sensitive photocatalyst.

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