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# Photocatalytic reduction of CO<sub>2</sub> with water using catalysts of $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> supported by $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>: mechanism and roles of each phase

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Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>), consisting of the mixed phases of  $\alpha$  and  $\beta$ ,  $\beta$  and  $\gamma$ , and  $\alpha$  and  $\gamma$ , is known as a photocatalyst for the reduction of CO<sub>2</sub> with water, producing CO, H<sub>2</sub> and O<sub>2</sub>. In previous studies, we investigated Ga<sub>2</sub>O<sub>3</sub> consisting of the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, systematically varying the contents of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> as catalysts for the photoreduction of CO<sub>2</sub> with water, and proposed a crude reaction mechanism of the photocatalytic reduction of CO<sub>2</sub>. However, the mechanism should be refined to clarify the roles of each phase and the effects of the morphology of the mixture. To do this, we have investigated the photocatalytic activity of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> supported by  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> instead of their mixed phases previously examined. With increasing contents of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, H<sub>2</sub> production rates monotonically decreased, whereas CO production rates increased, reached a maximum at 60–80% of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, and decreased significantly. These trends are consistent with those observed in the previous studies using the mixed phases. Based on the previously suggested mechanism, we have proposed the detailed mechanism as follows: (1) the surfaces of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles are hydro-oxidated to GaOOH in water, and GaOOH on the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles absorbs CO<sub>2</sub> as bicarbonate; (2) GaOOH on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is photo-decomposed to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> producing H; (3) the produced H migrates to the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles and reduces the adsorbed bicarbonate to CO; and (4) without UV photons, the surfaces of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> return to their initial states of GaOOH and bicarbonate-absorbing state, respectively.

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## Introduction

Ga<sub>2</sub>O<sub>3</sub> is well known as a photocatalyst for CO<sub>2</sub> reduction with water. Among its several different crystalline phases, the  $\alpha$ ,  $\beta$ , or  $\gamma$  phases have been used in most previous studies. In order to increase the production rate and selectivity of CO among CO<sub>2</sub> reduction products, metallic cocatalysts such as Ag (ref. 1–5) and others<sup>6–8</sup> have often been employed. In our previous work, it has been shown that mixed phases of  $\alpha$  and  $\beta$ ,<sup>9</sup>  $\alpha$  and  $\gamma$ ,<sup>10</sup> and  $\beta$  and  $\gamma$ <sup>11</sup> exhibit high photocatalytic activity without the co-catalysts.

In previous work<sup>10</sup> reporting a detailed investigation of the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> as the photocatalyst of the CO<sub>2</sub> reduction with water, we have suggested the CO<sub>2</sub> reduction mechanism such that water splitting dominates on

$\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and its H product reduces CO<sub>2</sub> adsorbed on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> to CO. However, in the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, it was difficult to control the morphology of the mixture and the particle sizes of both phases.

In order to verify the mechanism, we have investigated the catalytic activity of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> supported by  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> for the photocatalytic CO<sub>2</sub> reduction with water instead of the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> previously examined. The supported catalysts made it easier to control the contents and morphology of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> with clear separation of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. Comparing the present results with the previous results obtained using the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, we confirm the previously suggested CO<sub>2</sub> reduction mechanism and also provide an improved version. Furthermore, the roles of each phase in the mixed phase samples of the previous work and the present supported samples have been clarified.

## Experimental

### Experimental procedures

$\gamma$ -Ga<sub>2</sub>O<sub>3</sub> supported by  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> photocatalysts (referred to as  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> hereafter) were synthesized by an

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impregnation method. Their  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents were determined by XAFS analysis, and their morphology (geometrical structure) was observed by transmission electron microscopy (TEM). Specific surface area was measured by the BET method. CO<sub>2</sub> adsorption on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> was also examined by temperature-programmed desorption (TPD). The photocatalytic CO<sub>2</sub> reduction with water under UV light illumination was carried out and analyzed in terms of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, the morphology, and the specific surface area.

### Catalysts preparation

At first, Ga(NO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O (KISHIDA Chemical Corporation, purity 99%) was dissolved in distilled water. Then,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> powders, prepared by the calcination of GaOOH at 450 °C for 4 h as reported by Li *et al.*,<sup>12</sup> were dispersed in the solution. The dispersed solution was dried up and calcined at 450 °C for 4 h in air, resulting in  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples. The contents of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> (the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents) in  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (nominal contents) were controlled by varying the amounts of Ga(NO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>.

### Photocatalytic CO<sub>2</sub> reduction with water under UV light irradiation

A sample (0.1 g) was dispersed in 100 mL of water with 0.5 M NaHCO<sub>3</sub> and stirred in a reaction cell made of quartz. CO<sub>2</sub> gas flowed into the reaction cell at 3 mL min<sup>-1</sup>. UV light was provided by a Xe lamp through a UV cold mirror. The intensity of the light was 35 mW cm<sup>-2</sup> at 254 ± 10 nm. The produced gases (mostly H<sub>2</sub>, CO, and O<sub>2</sub>) were quantified by a gas chromatograph (TCD-GC, Shimadzu GC 8A). The reactions were monitored over five hours to confirm the steady-state production rates of H<sub>2</sub> and CO, which were determined every one hour.

### Characterization

The morphology of the samples was observed by TEM, and their specific surface areas were determined by the BET method. Their crystalline structures were determined by X-ray diffraction (XRD) analysis. X-ray absorption analyses (XANES/EXAFS) were also employed and used to determine the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents of the samples.

TEM images were observed with JEM-1000K RS (JEOL Ltd.) under an acceleration voltage of 1000 kV at the High Voltage Electron Microscope Laboratory in Nagoya University. XRD patterns were recorded on Rigaku MiniFlex 600 (Cu K $\alpha$  radiation, 40 kV, 15 mA) at room temperature. Ga K-edge XANES/EXAFS spectra were measured by the transmission method at room temperature at the 5S1 and 11S2 beam lines at Aichi Synchrotron Radiation Center. The ionization chambers were filled with 100% N<sub>2</sub> for incident X-rays (*I*<sub>0</sub>) and 50% N<sub>2</sub> and 50% Ar for transmitted X-rays (*I*). Powder samples were set on a masking tape to be thick enough to measure XANES/EXAFS. Specific surface areas were determined by the BET method with N<sub>2</sub> adsorption at -196 °C using a Monosorb™ (Quantachrome). Samples were

outgassed at 300 °C for 30 min under N<sub>2</sub> gas flow before measurement. FT-IR spectra were recorded with FT/IR-6100 (JASCO Co.) in the transmission mode at room temperature. Before the measurement, the sample was heated at 400 °C for 1 h. Temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was carried out as follows. After drying the sample (50 mg) under He gas flow (50 mL min<sup>-1</sup>) at 400 °C for 1 h, CO<sub>2</sub> was adsorbed under pure CO<sub>2</sub> gas flow at 40 °C for 1 h. Changing the CO<sub>2</sub> gas flow to a He gas flow (30 mL min<sup>-1</sup>), CO<sub>2</sub> desorption profiles of the samples were measured, while increasing the temperature from 40 °C to 600 °C at a heating rate of 10 °C min<sup>-1</sup>.

## Results

### TEM

Fig. 1 shows the TEM images and the electron diffraction patterns of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (a),  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> (b), and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples (c) and (d). The nominal  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents of the last two were 30% and 60%, respectively. As seen in Fig. 1(a),  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> consisted of columnar-shaped particles with the length and width of about 1  $\mu$ m and 0.5  $\mu$ m, respectively, and each particle was fully crystallized as seen in clear diffraction spots. In contrast, as shown in Fig. 1(b),  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> was composed of aggregates of nm-sized fine particles that were not well crystallized, giving halo rings without any clear spots of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>.  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples (Fig. (c) and (d)) clearly show that fine  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles exhibiting a halo ring were deposited on the larger columnar-shaped  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles showing clear diffraction spots. With increasing  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, the coverage of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles over the

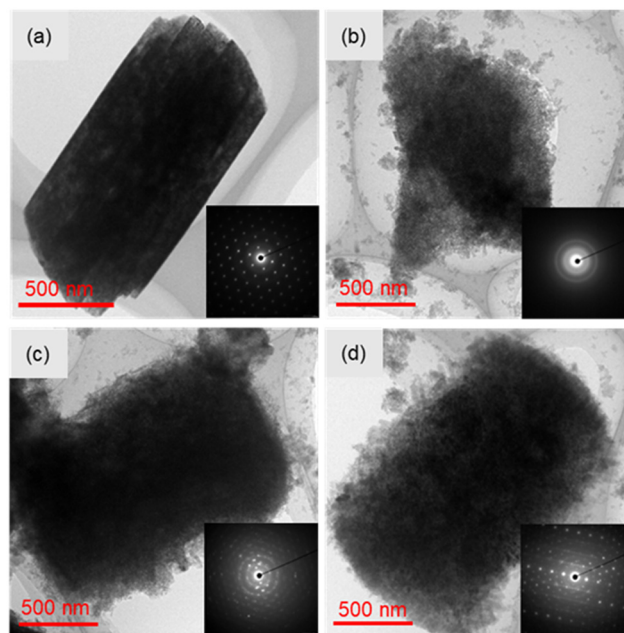


Fig. 1 TEM images and electron diffraction patterns of (a)  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, (b)  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, (c)  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $\gamma$  = 30%), and (d)  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $\gamma$  = 60%).



$\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles increased, but the sizes of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles hardly changed. In Fig. 1(d), the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particle was mostly covered by the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles.

### XRD

Fig. 2(a) and (b) show the XRD patterns of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> before and after use for the CO<sub>2</sub> reduction, respectively. Most of the sharp peaks were attributed to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, whereas those attributed to  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> were broad, indicating that the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is well crystallized, while the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> is poorly crystallized. This corresponds well to the diffraction patterns appearing in Fig. 1. For  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, the sharp peaks of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and the broad peaks of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> overlapped. Thus,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>—consisting of poorly crystallized fine  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles supported by larger, fully crystallized  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles—was synthesized.

As indicated in Fig. 2(b), new peaks appearing in the XRD patterns of the samples after use were attributed to GaOOH. This suggests that the surfaces of Ga<sub>2</sub>O<sub>3</sub> particles after use

were covered by GaOOH. Such hydro-oxidation of the surface of Ga<sub>2</sub>O<sub>3</sub> used as a photocatalyst for CO<sub>2</sub> reduction was reported in previous studies.<sup>9,10</sup>

### XAFS

Fig. 3(a) presents the Ga K-edge XANES spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. The differences in XANES fine structures among them were appreciable in the energy range of 10380–10480 eV, as shown in the enlarged inset. This allowed us to determine the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content of the samples as described below. Fig. 3(b) shows an example of the fitting. The fitted spectrum reproduces the experimental spectrum well, giving the compositions of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> phases of 58% and 42%, respectively.

Fig. 4(a) presents Ga K-edge EXAFS spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, showing clear differences in amplitude and periodicity among the three. This made us apply linear combination fitting used in XANES analysis to

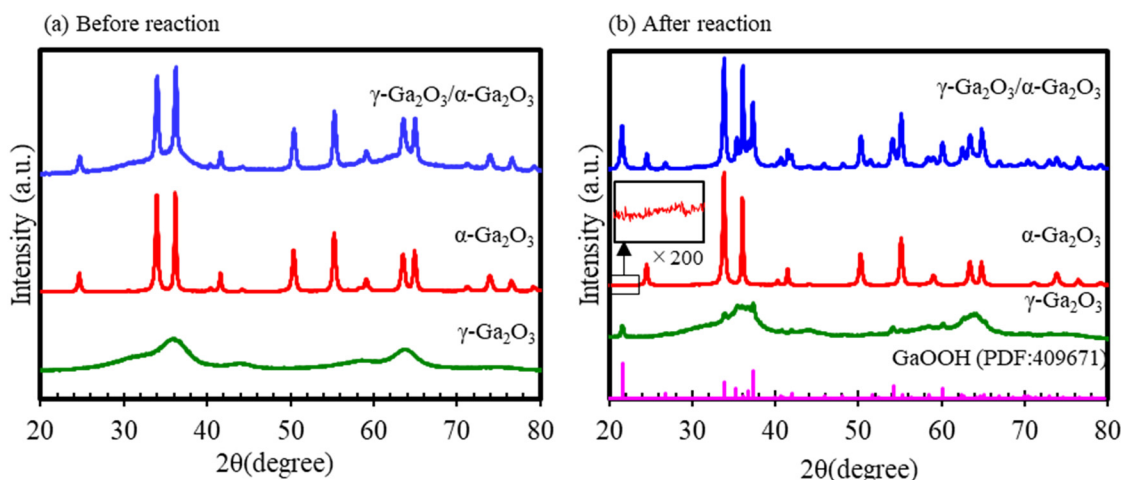


Fig. 2 XRD patterns of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> before (a) and after (b) the reaction. The inset is an enlarged view of the lower-angle side of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> spectrum to show the appearance of GaOOH.

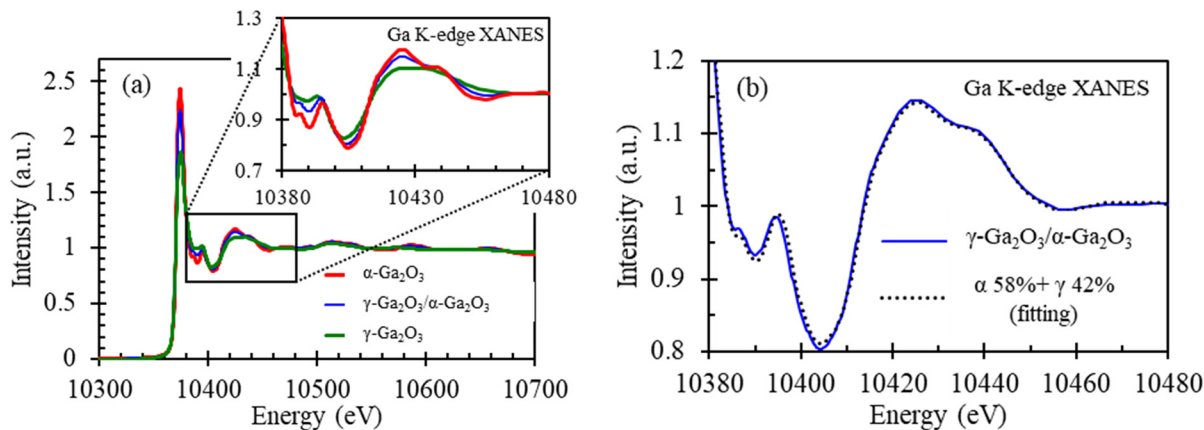
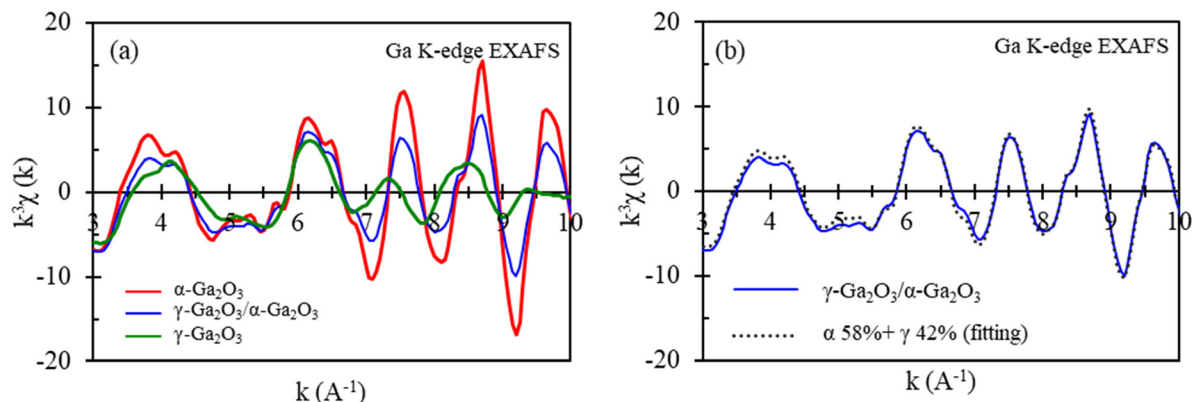


Fig. 3 (a) Ga K-edge XANES spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples. (b) Least squares fitting to the observed XANES spectra with a linear combination of the spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (58%) and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> (42%).





**Fig. 4** (a) Ga K-edge EXAFS spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples. (b) Least squares fitting to the observed EXAFS spectra with a linear combination of the spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (58%) and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> (42%).

**Table 1** Comparison of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents determined by least squares fitting using XANES and EXAFS spectra and the nominal states determined for all  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> samples

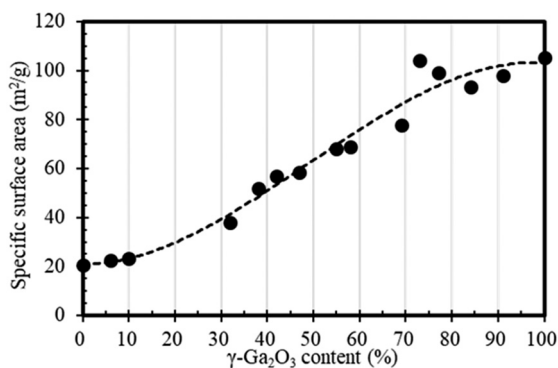
Amount of charge $\gamma$ (%)	10	20	30	40	50	53	56	60	70	80	83	86	90
Measured $\gamma$													
XANES (%)	6	10	32	38	42	47	55	58	69	73	77	84	91
EXAFS (%)	6	10	31	35	43	47	52	55	68	75	79	83	93

determine the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents. Fig. 4(b) shows an example of the fitting with the compositions of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> phases of 58% and 42%, respectively.

In Table 1, thus determined  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents by the XANES and EXAFS analyses are compared with the nominal  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents calculated by the mixing ratio of reagents for the synthesis. The determined values agreed within a difference of 3% for all samples.

### BET specific surface area

Fig. 5 shows the specific surface areas (SSAs) of all samples determined by the BET method as a function of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content determined by XANES analysis.  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> exhibited a much larger SSA than that of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. This is quite reasonable considering the poor crystallinity of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>. The SSA of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> increased with an S-shaped curve



**Fig. 5** Changes in BET specific surface area with  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content (dashed lines serve as a guide to the eyes).

showing a slower SSA increase at lower  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, a roughly linear increase in the middle range, and saturation over 70% of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content. This is different from the linear increase in SSA with the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents for the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> observed in the previous work.<sup>10</sup>

This S-shaped SSA increase corresponds well to the TEM observation. At the low  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents, nano-sized  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles were deposited discretely without appreciable increase in SSA. In the middle range of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, both SSA and the coverage of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles, which have a much larger SSA than that of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles, increased linearly until the surface of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles was mostly covered over 70% of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content.

### Photocatalytic reduction of CO<sub>2</sub> with water

The reaction products were mostly H<sub>2</sub>, CO, and O<sub>2</sub> for all samples. In Fig. 6, the production rates of H<sub>2</sub> and CO against the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents of the samples are plotted. The H<sub>2</sub> production rate was highest for  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and decreased monotonously with increasing  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content. This is quite consistent with our previous work using the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> and confirms that the H<sub>2</sub> production is dominated on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. The CO production rates stayed small for lower  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents, reached a maximum for samples containing 60–80% of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and then decreased markedly for higher  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents. This indicates that CO production is promoted by  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and that the existence of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is necessary; that is,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> alone (without  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>) showed little activity for the photocatalytic CO<sub>2</sub> reduction with water.



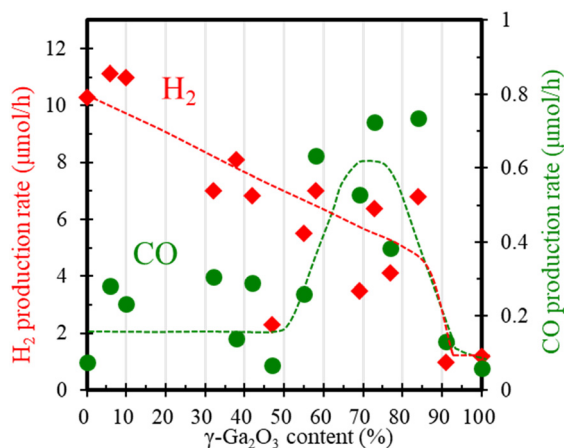


Fig. 6 Production rates of H<sub>2</sub> and CO plotted against the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (dashed lines serve as a guide to the eyes).

### CO<sub>2</sub>-TPD

Fig. 7 shows the CO<sub>2</sub>-TPD profiles of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $\gamma = 77\%$ ) in the temperature range from 200 °C to 600 °C. Although a desorption peak caused by the adsorbed water appeared under 200 °C, it is not shown in the figure. The adsorbed amounts of CO<sub>2</sub> on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> were similar and significantly larger than that on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. This indicates that CO<sub>2</sub> adsorption on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> mostly originated from  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>.

Considering that CO<sub>2</sub> adsorbed on Ga<sub>2</sub>O<sub>3</sub> is known to take mainly two species of carbonate and bicarbonate,<sup>13</sup> the two dominant peaks appeared at around 200–300 °C and 400–500 °C could be attributed to the former and the latter, respectively. This agrees with previous reports showing that, as the precursor of CO forms, the bicarbonate desorbing at higher temperature is more favorable than the carbonate.<sup>13–15</sup> The bicarbonate should be formed through the interaction of CO<sub>2</sub> with OH species on the Ga<sub>2</sub>O<sub>3</sub> surface. As depicted in Fig. 2(b), the surface of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> was converted to GaOOH, which very likely enhanced CO<sub>2</sub> adsorption as the bicarbonate (see (1)).

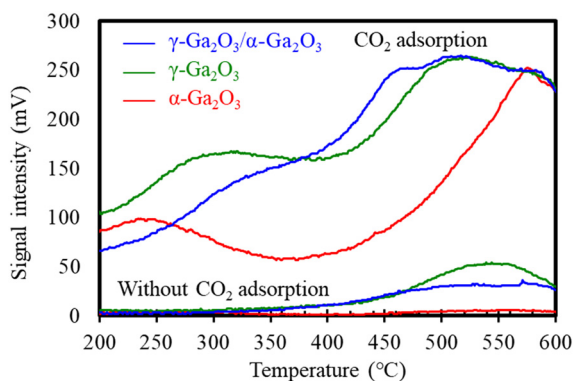
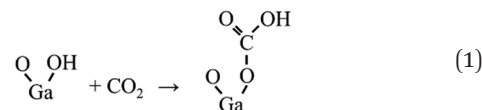


Fig. 7 CO<sub>2</sub>-TPD profiles for  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $\gamma = 77\%$ ) samples.



## Discussion

### Reaction mechanism

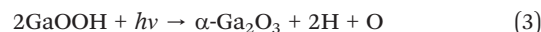
Here, we discuss the mechanism of the photocatalytic CO<sub>2</sub> reduction with water on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. As seen in Fig. 6, H<sub>2</sub> production was dominated on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, while CO production rates increased with the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents and reached a maximum for the samples containing 60–80% of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents. This observation is quite consistent with the previous work using the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>.<sup>10</sup> Considering the mechanism suggested in the previous work,<sup>10</sup> we have claimed a slightly more detailed mechanism as follows.

I. The surfaces of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles are hydroxylated to GaOOH in water,



and GaOOH on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles absorbs CO<sub>2</sub> a bicarbonate.

II. GaOOH on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is photo-decomposed to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, producing H, as reported by Aoki *et al.*<sup>9</sup>



III. The produced H migrates to the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles and reduces the adsorbed bicarbonate, resulting in CO. (It is not clear whether this process is photo-assisted or not).

IV. Without photons, the surfaces of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> return to their initial states of GaOOH and the bicarbonate-absorbing state, respectively.

This mechanism is schematically illustrated in Fig. 8.

### Effect of sample morphology on the reaction rate

Although the present results are quite similar to those observed in the previous work using the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, the present production rates of H<sub>2</sub> and CO were clearly smaller. As seen in Fig. 5, the SSA shows an S-shaped increase with  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, while a linear increase was observed in previous work. This seems reasonable considering the morphology difference, whereby

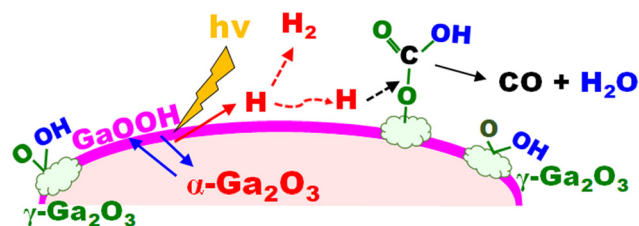


Fig. 8 Schematic drawing of the mechanism of photocatalytic CO<sub>2</sub> reduction with water on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>.



the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles cover the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles in the present work, while  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles were mixed in the previous work. The CO production rates of both studies were hardly correlated with the SSA. This also supports the reaction mechanism described above.

In the present work, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content giving the maximum production rate of CO was around 70%, which was clearly higher than 40% from the previous work, while 0.8 mmol h<sup>-1</sup> g<sup>-1</sup> of the former was clearly less than 3 mmol h<sup>-1</sup> g<sup>-1</sup> of the latter. This difference could be attributed to the difference in morphology between the supported  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>. Since in the former, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles cover the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> columnar particles, the surface area of the  $\alpha$  particles was comparatively less than that of the latter, resulting in less H production and, consequently, less CO production. In addition, in lower  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content samples of the former, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles covered the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> columnar particles rather discretely. Hence, H produced on the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles should migrate a longer distance compared with the mixed-phase samples, resulting in less CO production.

There is another geometrical factor. In the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples, both phases are directly exposed to the UV light, whereas in the supported  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> photocatalyst, the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles are partially or fully covered by the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles. In addition, owing to the smaller band gap of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles covering the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles would shield the UV light from the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particle beneath,<sup>16–18</sup> and thus reduce the H formation on the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles and consequently lead to lower CO production. These morphological effects further support the proposed reaction mechanism and emphasize the importance of phase arrangement and morphology in determining photocatalytic performance.

## Conclusions

In this work,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> supported by  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>) photocatalysts with different  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> contents were synthesized by impregnation followed by calcination. TEM and XRD analysis showed that nano-sized  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles were deposited on the surface of columnar-shaped  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particles. The  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content was successfully determined by Ga K-edge XAFS analysis.

Photocatalytic CO<sub>2</sub> reduction with water was carried out to investigate the change in H<sub>2</sub> and CO production rates with  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content. The H<sub>2</sub> production rate decreased with the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content, whereas the CO production rate reached a maximum at 60–80% of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content. These results indicate that H<sub>2</sub> production is dominated on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, while CO production is promoted on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, which absorbs a much larger amount of CO<sub>2</sub> in the form of bicarbonate compared to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>.

The changes in the production rates of CO and H<sub>2</sub> with  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> content are consistent with previous work using the

mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> as photocatalysts. Based on the previously suggested mechanism, a slightly more detailed mechanism is given as follows: (1) the surface of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles are hydro-oxidated to GaOOH in water, and GaOOH on the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles absorbs CO<sub>2</sub> as bicarbonate; (2) GaOOH on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is photo-decomposed to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, producing H; (3) the produced H migrates to the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles and reduces the adsorbed bicarbonate to CO. Without UV photons, the surfaces of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> return to their initial states of GaOOH and bicarbonate-absorbing state, respectively; and (4) without UV photons, the surfaces of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> return to GaOOH and bicarbonate-absorbing states, respectively. Still, the detailed pathways of CO production are unclear and need to be further researched.

Compared with the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> photocatalyst reported in the previous study, both H<sub>2</sub> and CO production rates of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> in the present study were lower. This difference is successfully attributed to the difference in the morphology, *i.e.*,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles covered the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> particle in the latter, while the mixed phases of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> particles in the former. These results demonstrate that not only phase composition but also the spatial arrangement of  $\alpha$  and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> plays a crucial role in controlling the CO<sub>2</sub> reduction activity of Ga<sub>2</sub>O<sub>3</sub>-based photocatalysts.

## Conflicts of interest

The authors declare no conflicts of interest.

## Data availability

Raw data were generated at Nagoya University. Derived data supporting the findings of this study are available from Tomoko Yoshida on request.

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