Analysis of Optical Properties and Structures of Nitrogen Doped Gallium Oxide*

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To promote photocatalytic activity of gallium oxides (Ga_2O_3) on CO_2 reduction with water under visible light irradiation, we have tried nitrogen doping into Ga_2O_3 with different crystalline structures. In diffuse reflectance UV-vis spectra, absorption bands appeared in the visible light region after the nitrogen doping and the absorption edge shifted to a longer wavelength region with increasing nitrogen doping temperature. N K-edge XANES analysis clearly showed two kinds of nitrogen species doped in the samples; gallium nitride (GaN) species and molecular like nitrogen. In XRD patterns, nitrogen doping at temperatures above 823 K, gallium nitride phases appeared while the original crystal structures of gallium oxide samples maintained when nitrogen doping temperature was less than 823 K. However, photocatalytic CO_2 reduction under visible light irradiation was insignificant for all the nitrogen doped samples, because nitrogen doped in Ga_2O_3 samples was unstable in water under the visible light irradiation. [DOI: 10.1380/ejssnt.2018.262]

Keywords: Gallium oxide; Nitriding; Visible light response; XAFS

I. INTRODUCTION

Photocatalytic CO_2 reduction with water has attracted much attention because of its potential to realize an artificial photosynthesis [1–3]. To use water as a reductant for CO_2 reduction, the activation of water is intrinsically required. Therefore, heterogeneous metal oxide photocatalysts which can activate water have been widely studied targeting CO_2 reduction with water [4–11]. Recently, Akatsuka *et al.* and Teramura *et al.* have found that gallium oxide (Ga_2O_3) shows photocatalytic activity for the CO_2 reduction with water producing CO under ultra violet (UV) light irradiation [5, 6, 12–14]. However, the

reduction was not observed under visible light irradiation because the band gap of Ga_2O_3 is too wide to absorb the visible light.

It is well known that only 6% or less energy of sunlight is given by UV light, while more than 50% by visible light [15]. For the efficient use of the sunlight energy, it is important to prepare photocatalysts driven by the visible light. Recently, it has been reported that nitrogen doping into metal oxides contributes to narrowing of their band gap, providing a visible-light response because N 2p orbitals are newly formed above O 2p orbitals in their valence band [16, 17]. To generate visible light response in Ga_2O_3 photocatalysts, we have tried nitrogen doping into Ga_2O_3 samples having different crystal structures. The results of the nitrogen doping, i.e., structural changes and the amount and chemical state of doped nitrogen were investigated by various analyzing techniques. Photocatalytic activity of the nitrogen doped samples for the CO_2 reduction with water under visible light irradiation was examined.

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FIG. 1. DR UV-vis spectra of CA-Ga₂O₃ and 873-Ga₂O₃ samples before and after nitrogen doping. A: (a) CA-Ga₂O₃, (b) CA-Ga₂O₃-823, (c) CA-Ga₂O₃-973, B: (a) 873-Ga₂O₃, (b) 873-Ga₂O₃-823, (c) 873-Ga₂O₃-873.

II. EXPERIMENTAL

A. Sample preparation

It has been reported that Ga₂O₃ prepared by calcination of gallium nitrate at around 800 K showed high photocatalytic activity for CO₂ reduction with water under UV light irradiation [18]. In this study, Ga₂O₃ samples were prepared by calcination of Ga(NO₃)₃·8H₂O (Kishida Chemical, 99.0%) in air at 873 K for 4 h. Thus obtained samples are referred to as 873-Ga₂O₃. Nitrogen doping was performed for 873-Ga₂O₃ and commercially available Ga₂O₃ (High Purity Chemicals, 99.99%, CA-Ga₂O₃) under continuous flow of NH₃ gas (50 mL min⁻¹). Nitrogen doping temperature and time for 873-Ga₂O₃ were 823 K or 873 K for 5 h, and those for CA-Ga₂O₃ were 823 K for 5 h or 973 K for 10 h. These samples are referred to as 873-Ga₂O₃-Y and CA-Ga₂O₃-Y (Y: nitrogen doping temperature), respectively.

B. Characterization

The crystalline structures of the nitrogen doped samples were investigated by X-ray diffraction (XRD) analysis. XRD patterns of the samples were recorded on a Mini-Flex600 (Rigaku) using Cu K α as the radiation source with an operating voltage of 40 kV and current of 15 mA. The XRD patterns were collected at 2 θ angles of 20–60°. The 2 θ step size was 0.02°, and the scanning rate was 10 degree/min.

Diffuse reflectance (DR) UV-visible spectra were measured using UV-visible spectrophotometer (JASCO, V-670). The spectra of BaSO₄ powder was used as the reference.

N K-edge and Ga K-edge XAFS measurements were carried out at BL7U and BL5S1 of Aichi Synchrotron Radiation Center, respectively. N K-edge XAFS spectra were measured in a total electron yield mode and Ga K-edge XAFS spectra in a transmission mode.

C. Photocatalytic CO₂ reduction

Photocatalytic CO₂ reduction with water was carried out using the nitrogen doped samples. Before the reac-

FIG. 2. N K-edge XANES spectra of (a) GaN (ref.), (b) CA-Ga₂O₃-973, (c) CA-Ga₂O₃-823, (d) 873-Ga₂O₃-873, (e) 873-Ga₂O₃-823.

tion, the sample (0.1 g) was exposed to visible-light generated by a 300 W Xe lamp with a cut filter for $\lambda > 420$ nm for 1 h under CO₂ gas with a flow rate of 3 mL/min, where the light intensity measured in the range of 415 ± 55 nm was 127 mW/cm^2 . Then a NaHCO₃ aqueous solution (H₂O 10 mL, NaHCO₃ 0.92 g) was added to the reactor cell in dark. After 1 h, the background in dark was measured with an online gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Shimadzu GC-8APT). Subsequently, photocatalytic reduction of CO₂ under the visible-light irradiation was started and CO, H₂, and O₂ production rates were measured for 5 h.

III. RESULTS AND DISCUSSION

A. Optical properties of nitrogen doped samples

Fig. 1 shows DR UV-vis spectra of CA-Ga₂O₃-Y and 873-Ga₂O₃-Y samples. Intensity of these spectra was converted to the Kubelka-Munk function. The DR spectra indicate that absorption bands appeared in the visible light region after the nitrogen doping. The absorption edge shifted to a longer wavelength region with increasing the temperature of nitrogen doping, suggesting the enhancement of the nitrogen doping at higher temperatures. It is noticeable that the absorption band in the visible light region was much smaller for CA-Ga₂O₃-823 compared with 873-Ga₂O₃-823, though both samples were nitrogen-doped at the same temperature. In the spectrum of 873-Ga₂O₃-873, the band shifted to 550 nm in a similar way to CA-Ga₂O₃-973. These results suggest that the 873-Ga₂O₃ includes larger amount of doped nitrogen than that for CA-Ga₂O₃.

B. Chemical states of doped nitrogen

N K-edge XANES spectra of the nitrogen doped samples shown in Fig. 2 confirm that the all samples contain nitrogen as the appearance of clear absorptions originated from σ and π bonds of nitrogen species [19, 20]. The chemical shifts or peak broadening of the XANES spectra

FIG. 3. X-ray diffraction patterns of CA-Ga₂O₃ and 873-Ga₂O₃ samples before and after nitrogen doping. A: (a) CA-Ga₂O₃-973, (b) CA-Ga₂O₃-823, (c) CA-Ga₂O₃, B: (a) 873-Ga₂O₃-873 (b) 873-Ga₂O₃-823 (c) 873-Ga₂O₃.

FIG. 4. Radial structure functions for Ga K-edge EXAFS spectra of CA-Ga₂O₃ and 873-Ga₂O₃ samples before and after the nitrogen doping. A: (a) CA-Ga₂O₃, (b) CA-Ga₂O₃-823, (c) CA-Ga₂O₃-973, (d) GaN reference, B: (a) 873-Ga₂O₃, (b) 873-Ga₂O₃-823, (c) 873-Ga₂O₃-873, (d) GaN reference.

and the redshift of absorption edge in DR UV-vis spectra reflect chemical nature of the doped nitrogen as discussed below.

The XANES features of the CA-Ga₂O₃-973, CA-Ga₂O₃-823 and 873-Ga₂O₃-873 [Fig. 2(b–d)] were similar to that of a GaN reference sample [Fig. 2(a)]. On the other hand, the XANES spectra of 873-Ga₂O₃-823, [Fig. 2(e)] exhibited a broad feature having a small peak around 400 eV. Metson *et al.* and Chiou *et al.* have reported that this peak corresponds to molecular nitrogen [19, 20]. Therefore, the 400 eV peak could be associated with the presence of interstitial molecular like nitrogen or small bubbles containing N₂. Thus, the XANES analysis indicates the existence of at least two different kinds of nitrogen chemical states in the samples; i.e., nitrogen bonded to Ga atom (Ga–N species) and molecular like nitrogen.

C. Structural analysis of Ga₂O₃ samples before and after the nitrogen doping

Fig. 3 shows X-ray diffraction patterns of CA-Ga₂O₃ and 873-Ga₂O₃ samples before and after the nitrogen doping. The crystalline structure of CA-Ga₂O₃ was assigned to β -phase Ga₂O₃. After the nitrogen doping, the original crystal structure maintained in CA-Ga₂O₃-823, while GaN phase dominated in CA-Ga₂O₃-973. The XRD pat-

tern of 873-Ga₂O₃ exhibited the broad diffraction peaks of γ -phase Ga₂O₃ together with some weak peaks attributed to β -phase Ga₂O₃, indicating the coexistence of the β - and γ -phases. The XRD pattern of 873-Ga₂O₃-823 was almost the same as that of 873-Ga₂O₃, whereas small diffraction peaks attributed to GaN phase were included in 873-Ga₂O₃-873. Thus, nitrogen doping at temperatures above 823 K induced the precipitation of GaN phase, while the original crystal structures fundamentally maintained in CA-Ga₂O₃ and 873-Ga₂O₃ samples when nitrogen doping temperatures were below 823 K.

The local structures of CA-Ga₂O₃ and 873-Ga₂O₃ samples before and after the nitrogen doping were also investigated by Ga K-edge EXAFS analysis. The Fourier transform was performed on each EXAFS spectrum in the range from 3 Å⁻¹ to 12 Å⁻¹ and the radial structure function (RSF) was obtained as shown in Fig. 4. Peak appeared at 1–2 Å is assigned to the backscattering from the adjacent oxygen (O) or nitrogen (N) atoms (Ga–O or Ga–N bond), and peaks around 3 Å show the presence of the second-neighboring gallium atoms [Ga–(O,N)–Ga bond]. The backscattering amplitude and phase shift of O and N are almost the same. This inhibits the distinction of Ga–O and Ga–N bonds and makes discussion about the formation of Ga–N bonds difficult. However, the changes in local structure were proposed by considering the XRD patterns given results in Fig. 3.

In the RSF of CA-Ga₂O₃, the peak around 3 Å at-

tributed to Ga–O–Ga bond was higher than the peak at 1–2 Å due to Ga–O bond [Fig. 4A(a)], which should be characteristic of the local structure of β -phase Ga_2O_3 . Although the RSF of CA- Ga_2O_3 was not changed by the nitrogen doping at 823 K [Fig. 4A(b)], a large peak around 3 Å newly appeared with the nitrogen doping at 923 K [Fig. 4A(c)]. This large peak is attributed to GaN structure (Ga–N–Ga bond), referring the RSF of commercially available GaN.

On the other hand, in RSF of 873- Ga_2O_3 in Fig. 4B whose crystalline structure was assigned to be mixture of γ and β phases of Ga_2O_3 as revealed from the XRD analysis, the peak at 1–2 Å is much higher than the peak around 3 Å. Nitrogen doping into 873- Ga_2O_3 samples reduced both peaks attributed to Ga–O and Ga–O–Ga bonds with more significant reduction in 873- Ga_2O_3 -823 compared with that in CA- Ga_2O_3 -823. This result suggests that the original local structure of 873- Ga_2O_3 changed since larger amount of Ga–N bonds were formed at higher nitrogen doping temperature.

As discussed above, XRD measurements suggested that both crystal structures of CA- Ga_2O_3 and 873- Ga_2O_3 samples fundamentally maintained after the nitrogen doping at 823 K. However, the local structure of 873- Ga_2O_3 already changed by introducing some amount of nitrogen molecules whereas the local structure of CA- Ga_2O_3 showed no remarkable change. Generally, it is well known that Ga_2O_3 is a so-called crystal polymorph, which could take five different crystal structures (α - Ga_2O_3 , β - Ga_2O_3 , γ - Ga_2O_3 , δ - Ga_2O_3 , and ε - Ga_2O_3). Among them, γ - Ga_2O_3 exhibits the defective amorphous-like phase, while β - Ga_2O_3 is the most stable phase [21, 22]. Therefore, the amount of doped nitrogen was larger in 873- Ga_2O_3 rather than that in CA- Ga_2O_3 . In CA- Ga_2O_3 , nitrogen would be introduced into β - Ga_2O_3 phase accompanying defects formation. Thus, defective structure such as γ - Ga_2O_3 rather than stable β - Ga_2O_3 structure allows larger amount of nitrogen doping.

D. Photocatalytic CO_2 reduction with water

Although photocatalytic CO_2 reduction with water under visible light irradiation was conducted using the ni-

trogen doped samples (823- Ga_2O_3 -Y and CA- Ga_2O_3 -Y), the photocatalytic activity was insignificant. Instead the color of the nitrogen doped samples changed from yellow to white. The color change suggests that the doped nitrogen atoms were oxidized by photogenerated holes and released from the samples ($2\text{N}^{3-} + 6\text{h}^+ \rightarrow \text{N}_2$) [23, 24]. In particular, the defective amorphous like γ - Ga_2O_3 phase might enhance the nitrogen evolution from the samples. Thus, the nitrogen doped Ga_2O_3 samples were unstable in water under the visible light irradiation, even if they had initially some activity for CO_2 reduction. Now we are trying to suppress the self-oxidation and nitrogen evolution of the samples.

IV. CONCLUSION

Based on our previous work indicating potential photocatalytic activity of Ga_2O_3 for CO_2 reduction with water under UV light irradiation, we have tried nitrogen doping into gallium oxide samples having different crystalline structures with using NH_3 in order to enhance their photocatalytic activity under visible light. The nitrogen doping was successfully done and optical properties were improved to absorb visible light. However, nitrogen doped into Ga_2O_3 samples was unstable in water under the visible light irradiation. Hence, photocatalytic CO_2 reduction under visible light irradiation was insignificant. Stabilization of doped nitrogen in Ga_2O_3 in water remains an important issue to resolve.

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