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

Yuma Kato†

Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Muneaki Yamamoto

Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Akiyo Ozawa

Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan and Corporate Research Laboratories, Research & Development Division, Sakai Chemical Industry Co., Ltd., 5-2, Ebisujima-cho, Sakai-ku, Sakai 590-0815, Japan

Yu Kawaguchi

Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Akinobu Miyoshi, Takayoshi Oshima, and Kazuhiko Maeda

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-NE-2 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Tomoko Yoshida

Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

(Received 12 January 2018; Accepted 5 May 2018; Published 14 June 2018)

To promote photocatalytic activity of gallium oxides (Ga$_2$O$_3$) on CO$_2$ reduction with water under visible light irradiation, we have tried nitrogen doping into Ga$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$) shows photocatalytic activity for the CO$_2$ reduction with water producing CO under ultraviolet (UV) light irradiation [5, 6, 12–14]. However, the reduction was not observed under visible light irradiation because the band gap of Ga$_2$O$_3$ 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$_2$O$_3$ photocatalysts, we have tried nitrogen doping into Ga$_2$O$_3$ 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.

* This paper was presented at the 11th International Symposium on Atomic Level Characterizations for New Materials and Devices '17, Aqua Kaiulani Beach Resort, Kanai, Hawaii, USA, December 3-8, 2017.
† Corresponding author: m17tc011@eb.osaka-cu.ac.jp
II. EXPERIMENTAL

A. Sample preparation

It has been reported that Ga$_2$O$_3$ prepared by calcination of gallium nitrate at around 800 K showed high photocatalytic activity for CO$_2$ reduction with water under UV light irradiation [18]. In this study, Ga$_2$O$_3$ samples were prepared by calcination of Ga(NO$_3$)$_3$·8H$_2$O (Kishida Chemical, 99.0%) in air at 873 K for 4 h. Thus obtained samples are referred to as 873-Ga$_2$O$_3$. Nitrogen doping was performed for 873-Ga$_2$O$_3$ and commercially available Ga$_2$O$_3$ (High Purity Chemicals, 99.99%, CA-Ga$_2$O$_3$) under continuous flow of NH$_3$ gas (50 mL min$^{-1}$). Nitrogen doping temperature and time for 873-Ga$_2$O$_3$ were 823 K or 873 K for 5 h, and those for CA-Ga$_2$O$_3$ were 823 K for 5 h or 973 K for 10 h. These samples are referred to as 873-Ga$_2$O$_3$-Y and CA-Ga$_2$O$_3$-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 Kα as the radiation source with an operating voltage of 40 kV and current of 15 mA. The XRD patterns were collected at 2θ angles of 20–60°. The 2θ 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 BaSO$_4$ 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 CO$_2$ reduction

Photocatalytic CO$_2$ reduction with water was carried out using the nitrogen doped samples. Before the reaction, the sample (0.1 g) was exposed to visible-light generated by a 300 W Xe lamp with a cut filter for λ > 420 nm for 1 h under CO$_2$ 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 NaHCO$_3$ aqueous solution (H$_2$O 10 mL, NaHCO$_3$ 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 CO$_2$ under the visible-light irradiation was started and CO, H$_2$, and O$_2$ 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-Ga$_2$O$_3$-Y and 873-Ga$_2$O$_3$-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-Ga$_2$O$_3$-823 compared with 873-Ga$_2$O$_3$-823, though both samples were nitrogen-doped at the same temperature. In the spectrum of 873-Ga$_2$O$_3$-873, the band shifted to 550 nm in a similar way to CA-Ga$_2$O$_3$-973. These results suggest that the 873-Ga$_2$O$_3$ includes larger amount of doped nitrogen than that for CA-Ga$_2$O$_3$.

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...
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-Ga$_2$O$_3$-973, CA-Ga$_2$O$_3$-823 and 873-Ga$_2$O$_3$-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-Ga$_2$O$_3$-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 N$_2$. 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 Ga$_2$O$_3$ samples before and after the nitrogen doping

Fig. 3 shows X-ray diffraction patterns of CA-Ga$_2$O$_3$ and 873-Ga$_2$O$_3$ samples before and after the nitrogen doping. The crystalline structure of CA-Ga$_2$O$_3$ was assigned to β-phase Ga$_2$O$_3$. After the nitrogen doping, the original crystal structure maintained in CA-Ga$_2$O$_3$-823, while GaN phase dominated in CA-Ga$_2$O$_3$-973. The XRD pattern of 873-Ga$_2$O$_3$ exhibited the broad diffraction peaks of γ-phase Ga$_2$O$_3$ together with some weak peaks attributed to β-phase Ga$_2$O$_3$, indicating the coexistence of the β- and γ-phases. The XRD pattern of 873-Ga$_2$O$_3$-823 was almost the same as that of 873-Ga$_2$O$_3$, whereas small diffraction peaks attributed to GaN phase were included in 873-Ga$_2$O$_3$-973. Thus, nitrogen doping at temperatures above 823 K induced the precipitation of GaN phase, while the original crystal structures fundamentally maintained in CA-Ga$_2$O$_3$ and 873-Ga$_2$O$_3$ samples when nitrogen doping temperatures were below 823 K.

The local structures of CA-Ga$_2$O$_3$ and 873-Ga$_2$O$_3$ 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-Ga$_2$O$_3$, 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 Ga2O3. Although the RSF of CA-Ga2O3 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-Ga2O3 in Fig. 4B whose crystalline structure was assigned to be mixture of γ and β phases of Ga2O3 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-Ga2O3 samples reduced both peaks attributed to Ga–O and Ga–O–Ga bonds with more significant reduction in 873-Ga2O3-823 compared with that in CA-Ga2O3-823. This result suggests that the original local structure of 873-Ga2O3 changed since the 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-Ga2O3 and 873-Ga2O3 samples fundamentally maintained after the nitrogen doping at 823 K. However, the local structure of 873-Ga2O3 already changed by introducing some amount of nitrogen molecules whereas the local structure of CA-Ga2O3 showed no remarkable change. Generally, it is well known that Ga2O3 is a so-called crystal polymorph, which could take five different crystal structures (α-Ga2O3, β-Ga2O3, γ-Ga2O3, ε-Ga2O3, and δ-Ga2O3). Among them, γ-Ga2O3 exhibits the defective amorphous-like phase, while β-Ga2O3 is the most stable phase [21, 22]. Therefore, the amount of doped nitrogen was larger in 873-Ga2O3 rather than that in CA-Ga2O3. In CA-Ga2O3, nitrogen would be introduced into β-Ga2O3 phase accompanying defects formation. Thus, defective structure such as γ-Ga2O3 rather than stable β-Ga2O3 structure allows larger amount of nitrogen doping.

D. Photocatalytic CO2 reduction with water

Although photocatalytic CO2 reduction with water under visible light irradiation was conducted using the nitrogen doped samples (823-Ga2O3-Y and CA-Ga2O3-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 (2N3+ + 6h+ → N2) [23, 24]. In particular, the defective amorphous like γ-Ga2O3 phase might enhance the nitrogen evolution from the samples. Thus, the nitrogen doped Ga2O3 samples were unstable in water under the visible light irradiation, even if they had initially some activity for CO2 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 Ga2O3 for CO2 reduction with water under UV light irradiation, we have tried nitrogen doping into gallium oxide samples having different crystalline structures with using NH3 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 Ga2O3 samples was unstable in water under the visible light irradiation. Hence, photocatalytic CO2 reduction under visible light irradiation was insignificant. Stabilization of doped nitrogen in Ga2O3 in water remains an important issue to resolve.

ACKNOWLEDGMENTS

This study was supported by JSPS KAKENHI Grant Numbers JP16H06440, JP16H06441, and JP16H06438 (Synthesis of Mixed Anion Compounds toward Novel Functionalities).

[1] J. L. G. Fierro, Catal. Lett. 22, 67 (1993).
[2] D. Chen, X. Zhang, and A. F. Lee, J. Mater. Chem. A 3, 14487 (2015).
[3] A. Kubacka, M. Fernandez-Garcia, and G. Colon, Chem. Rev. 112, 1555 (2012).
[4] K. Izuka, T. Wato, Y. Miseki, K. Saito, and A. Kudo, J. Am. Chem. Soc. 133, 20863 (2011).
[5] M. Akatsuka, T. Yoshiida, N. Yamamoto, M. Yamamoto, S. Ogawa, and S. Yagi, J. Phys.: Conf. Ser. 712, 012056 (2016).
[6] K. Teramura, Z. Wang, S. Hosokawa, Y. Sakata, and T. Tanaka, Chem. Eur. J. 20, 9906 (2014).
[7] Z. Wang, K. Teramura, S. Hosokawa, and T. Tanaka, J. Mater. Chem. A 3, 11313 (2015).
[8] T. Takayama, K. Tanabe, K. Saito, A. Iwase, and A. Kudo, Phys. Chem. Chem. Phys. 16, 24417 (2014).
[9] T. Takayama, A. Iwase, and A. Kudo, Bull. Chem. Soc. Jpn. 88, 538 (2015).
[10] Z. Wang, K. Teramura, S. Hosokawa, and T. Tanaka, Appl. Catal. B 163, 241 (2015).
[11] H. Yoshiida, L. Zhang, M. Sato, T. Morikawa, T. Kajino, T. Sekito, S. Matsumoto, and H. Hirata, Catal. Today 251, 132 (2015).
[12] N. Yamamoto, T. Yoshiida, S. Yagi, Z. Like, T. Mizutani, S. Ogawa, H. Nameki, and H. Yoshiida, e-J. Surf. Sci. Nanotech. 12, 263 (2014).
[13] M. Yamamoto, T. Yoshiida, N. Yamamoto, T. Nomoto, A. Yamamoto, H. Yoshiida, and S. Yagi, J. Phys.: Conf. Ser. 712, 012074 (2016).
[14] M. Yamamoto, T. Yoshiida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi, and H. Yoshiida, J. Mater. Chem. A 3, 16810 (2015).
[15] A. Nakada, T. Nakashima, K. Sekizawa, K. Maeda, and O. Ishitani, Chem. Sci. 7, 4364 (2016).
[16] R. Asahi, T. Owaki, K. Aoki, and Y. Taga, Science 293, 269 (2001).
[17] R. Asahi and T. Morikawa, Chem. Phys. 339, 57 (2007).
[18] Y. Kawaguchi, M. Akatsuka, M. Yamamoto, K. Yoshioka, A. Ozawa, Y. Kato, and T. Yoshiida, J. Photochem. Photobiol. A 358, 459 (2018).
[19] J. B. Metson, H. J. Trodahl, B. J. Ruck, U. D. Lanke, and A. Bittar, Surf. Interface Anal. 35, 719 (2003).
[20] J. W. Chiou, J. C. Jan, H. M. Tsai, and W. F. Ponga, Appl. Phys. Lett. 82, 3949 (2003).
[21] R. Roy, V. G. Hill, and E. F. Osborn, J. Am. Chem. Soc. 74, 719 (1952).
[22] L. Li, W. Wei, and M. Behrens, Solid State Sci. 14, 971 (2012).
[23] G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, Chem. Commun. 1698 (2002).
[24] M. Higashi, K. Domen, and R. Abe, J. Am. Chem. Soc. 134, 6968 (2012).