Nitrogen doping into gallium oxide hydroxide for the preparation of visible light response photocatalyst

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Abstract: In order to generate photocatalytic activity under visible light irradiation, we have tried nitrogen doping of gallium oxide hydroxide to produce gallium oxynitride (GaON), which can absorb visible light. UV-vis diffuse reflectance and N K-edge XANES spectra showed that prepared GaON samples contained nitrogen after nitrogen doping. With increasing nitrogen doping temperature, the samples showed higher crystallinity and above 973K gallium nitride (GaN) precipitated. The GaON sample prepared by nitrogen doping at 1173 K showed catalytic activity for H_2 evolution from a methanol aqueous solution under visible light irradiation, while commercially available GaN sample did not.

Keywords: Gallium oxynitride, Photocatalyst, H_2 evolution

1. Introduction

Recently, it has been reported that gallium oxide (Ga_2O_3) showed photocatalytic activity for water splitting and carbon dioxide (CO_2) reduction with water under ultra violet (UV) light irradiation [1]. In order to generate visible light response in Ga_2O_3 photocatalysts, we tried nitrogen doping of Ga_2O_3 by calcination under ammonia (NH_3) atmosphere in our previous study. However, even H_2 evolution from water using methanol solution as a sacrificial reagent did not proceed over the nitrogen doped Ga_2O_3 under visible light irradiation. In this study, gallium oxynitride (GaON) samples were prepared by calcination gallium oxide hydroxide (GaOOH), a precursor of Ga_2O_3, under NH_3 atmosphere. We analyzed optical properties and structures of the prepared GaON samples and examined whether they promote H_2 evolution from a methanol aqueous solution under visible light irradiation.

2. Experimental

GaOOH powder was obtained by autoclaving of ammonium solution including gallium nitrate at 120 °C for 6 h, followed by filtration and drying. Nitrogen doping of GaOOH was performed by calcination under NH_3 flow at various temperatures, as summarized in Table 1. The prepared samples (referred as GaON) were characterized by Field Emission-Scanning electron microscopy (FE-SEM), UV-vis diffuse reflectance (DR), powder X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) and X-ray photoelectron (XP) spectroscopies. We carried out H_2 evolution reactions from methanol 20 vol% aqueous solution under visible light irradiation (λ>420 nm), using 0.5 wt % Pt co-catalyst loaded the GaON samples.

3. Results and discussion

Figure 1 showed SEM images of the samples (a) and (f) referred in Table 1. The particle shape of the sample (a) was a rod-like shape with rather smooth surfaces. On the other hand, the appearance of sample (f) was quite rough and hard to distinguish particles. UV-vis DR measurements of the prepared samples indicated that absorption bands appeared in the visible light region after nitrogen doping. N K-edge XANES spectra of the samples showed the peaks attributed to σ and π bonds of nitrogen species, indicating that the nitrogen doping was

Table 1. Nitriding condition of GaOOH.

Entry	temp (K)	time (h)	NH_3 flow rate (mL/min)
(a)[1]	-	-	-
(b)	773	15	60
(c)	873	15	60
(d)	973	15	60
(e)	1073	15	60
(f)	1173	15	60
(g)[2]	-	-	-

[1]GaOOH, [2]GaN (reference samples)

successfully done. As shown in Fig.2, XANES spectral profiles represented the chemical states of nitrogen. The XANES features of sample (e) and (f) were similar to that of a GaN reference sample. On the other hand, the XANES spectra of sample (b)-(d) 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 [2, 3]. Therefore, the 400 eV peak was associated with the presence of molecular like nitrogen or small bubbles containing N_2. Thus, we confirmed that molecular nitrogen existed as interstitials when nitrogen doping temperature was under 973 K.

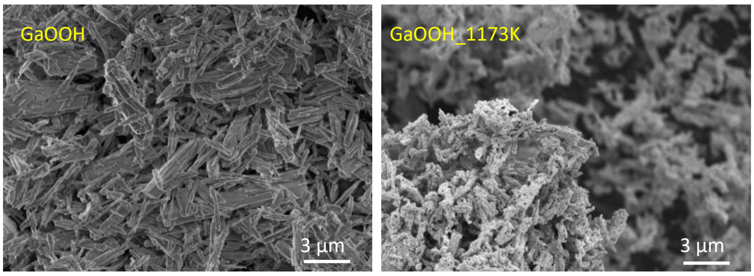

Figure 1. SEM images of sample (a) and (f)

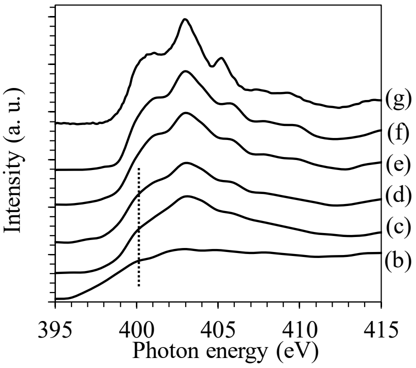

Figure 2. N K-edge XANES spectra of sample (b)-(g)

We also investigated bulk and local crystalline structures by XRD and Ga K-edge EXAFS measurements. In XRD patterns of the samples nitrogen-doped above 973 K, gallium nitride (GaN) phase started to appear, and the samples had higher crystallinity with increased nitrogen doping temperature. Similar results were obtained from the Ga K-edge EXAFS measurement. However, radial structure functions of prepared samples (e) and (f) were a little different from that that of commercially available GaN (g), suggesting that some Ga-O bonds is remained (Fig.3).

H_2 evolution reactions using prepared samples were performed under visible light irradiation (λ>420 nm). This reaction did not proceed over commercially available GaN and prepared samples (b)-(e) while the sample (f) promoted H_2 evolution. XRD measurements before and after the reaction revealed that bulk crystalline structure of the sample (f) fundamentally maintained while those of samples (b)-(e) had changed probably due to release of doped nitrogen. This result suggested that sample (f) could promote H_2 evolution reaction because the doped nitrogen would not be released during the reaction.

4. Conclusions

In order to generate visible light response in Ga_2O_3 photocatalysts which proceeded CO_2 reduction with water under UV light irradiation, gallium oxynitride (GaON) samples were prepared by nitrogen doping of gallium oxide hydroxide (GaOOH) as a precursor of Ga_2O_3. The nitrogen doping was successfully done and optical properties were improved to absorb visible light. The sample prepared by nitrogen doping at the highest temperature (1173 K), showed visible light response to produce H_2 from methanol aqueous solution while the other samples did not. The former sample could show H_2 evolution activity since it's original crystalline structure was maintained after the reaction whereas the other samples had changed their structures by releasing doped nitrogen.

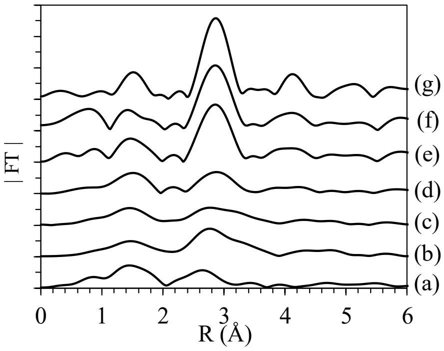

Figure 3. Radial structure functions for Ga K-edge EXAFS spectra of sample (a)-(g).

References

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