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Growth and Photocatalytic Properties of Gallium Oxide Films Using Chemical Bath Deposition

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Abstract: Gallium oxide (Ga_2O_3) thin films were fabricated on glass substrates using a combination of chemical bath deposition and post-annealing process. From the field-emission scanning electron microscopy and x-ray diffraction results, the GaOOH nanorods precursors with better crystallinity can be achieved under higher concentrations (≥ 0.05 M) of gallium nitrate ($\text{Ga}(\text{NO}_3)_3$). It was found that the GaOOH synthesized from lower $\text{Ga}(\text{NO}_3)_3$ concentration did not transform into α - Ga_2O_3 among the annealing temperatures used (400–600 °C). Under higher $\text{Ga}(\text{NO}_3)_3$ concentrations (≥ 0.05 M) with higher annealing temperatures (≥ 500 °C), the GaOOH can be transformed into the Ga_2O_3 film successfully. An α - Ga_2O_3 sample synthesized in a mixed solution of 0.075 M $\text{Ga}(\text{NO}_3)_3$ and 0.5 M hexamethylenetetramine exhibited optimum crystallinity after annealing at 500 °C, where the α - Ga_2O_3 nanostructure film showed the highest aspect ratio of 5.23. As a result, the photodegradation efficiencies of the α - Ga_2O_3 film for the methylene blue aqueous solution can reach 90%.

Keywords: Ga_2O_3 ; GaOOH; chemical bath deposition; photocatalytic property

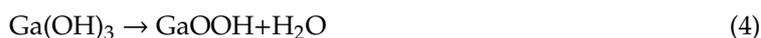
1. Introduction

Environmental protection, especially against water pollution, has generated public interest in recent years, and the application of nanotechnology in this field has become a hot topic. Photocatalysis using natural sunlight as a clean energy source, has been extensively studied for environmental remediation since its discovery [1–4]. Methylene blue (MB), a common dye, has been widely used for the commercial products such as the dyeing paper, linen, silk fabric, bamboo, wood, etc. The discharge of untreated MB into the wastewater can lead to serious pollution problems, making degradation and decolorization of MB is one of the important targets of dyeing wastewater treatment [5,6].

Metal oxides, such as titanium dioxide, zinc oxide, and gallium oxide (Ga_2O_3), are considered promising for photocatalytic applications due to their excellent physical and chemical properties [7–11]. Among these metal oxides, Ga_2O_3 , with various polymorphs (α -, β -, γ -, δ -, and ϵ -) can be synthesized at different temperatures [12,13]. Gallium oxides, which have wide bandgap ranging from 4.2 to 4.9 eV, are particularly important semiconductor materials [11,14]. The Ga_2O_3 material can be used for various device applications, such as gas sensors [15], catalysis [16], power and high voltage electronic

devices [13] because it has unique conductive properties and is electrically and thermodynamically stable [17–19]. Various polymorphs of Ga₂O₃ as the photocatalysts in the degradation of organic dyes have been studied previously [11,20–22]. Reddy et al. [11] have reported that the photodegradation efficiencies of α-Ga₂O₃ and β-Ga₂O₃ nanorods for the rhodamine B aqueous solution were 62% and 79%, respectively. The photocatalytic activity of α-Ga₂O₃ in the malachite green degradation was studied by Rodríguez et al. [20]. Zhao et al. [21], have demonstrated that the photodegradation efficiency of β-Ga₂O₃ nanorods in the perfluorooctanoic acid can reach 98.8%. In addition, the photocatalytic activity of the γ-Ga₂O₃ in rhodamine 590 degradation has also been investigated by Jin et al. [22].

Recently, various methods have been used to synthesize Ga₂O₃, including hydrothermal techniques [11,23], microwave-assisted hydrothermal methods [21], sol-gel methods [24], spray pyrolysis processes [25], and chemical vapor deposition [26]. The advantages of CBD for the synthesis of metal oxide thin films are based on the relatively low cost and convenience for deposition over a large area [27]. However, there are very few reports on the synthesis of Ga₂O₃ thin films via CBD. In this study, the Ga₂O₃ thin films were synthesized on the glass substrates using CBD with various post annealing treatments. The chemistry of the synthesis process can be summarized as follows [20,28–30]:



2. Experimental

Ga₂O₃ thin films were prepared on glass substrates using CBD. Analytical grade gallium (III) nitrate hydrate (Ga(NO₃)₃·nH₂O, 99.9%) and hexamethylenetetramine (HMT, 99.9%) were used as starting materials. The glass substrates were cleaned with acetone, methanol, and 10% hydrofluoric acid for 10 min respectively, then rinsed with deionized (DI) water. Three growth solutions were prepared by dissolving 0.025 mol, 0.05 mol, or 0.075 mol Ga(NO₃)₃ and 0.5 mol HMT in 1 L of DI water. To obtain the GaOOH precursor, each aqueous solution was placed in a beaker with a glass substrate and vigorously stirred at 500 rpm with a magnetic stirrer for 5 h at 95 °C. The precursor was then dried at 70 °C for 5 min and allowed to cool naturally to room temperature. The as-prepared GaOOH thin films were annealed in a furnace tube at either 400 °C, 500 °C, or 600 °C for 3 h to form Ga₂O₃ thin films.

The crystal structures of the as-prepared samples were characterized using a high resolution X-ray diffraction system (HR-XRD, X'Pert Pro MRD, PANalytical, Almelo, Nederland). A JSM-6700F field-emission scanning electron microscope (FE-SEM, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS) was used to analyze the morphologies of the samples and their elemental distributions. FT-IR spectra were collected in the range from 4000 to 500 cm⁻¹ with a Vertex 80v Fourier transform infrared spectrometer (Bruker, Billerica, Massachusetts, MA, USA). The photocatalytic properties of the Ga₂O₃ thin films in aqueous MB solutions were evaluated during and after irradiation under an 8 W UV lamp at wavelengths from 100 to 280 nm. Thin films with dimensions of 1 cm × 1 cm were first placed in aqueous solutions containing 5 ppm MB. The solutions were then irradiated for 5 h at room temperature in an otherwise dark environment. Photodegradation efficiency was determined through UV-visible spectrophotometric analysis (U3010, Hitachi, Tokyo, Japan)

3. Results and Discussion

The FE-SEM images of the GaOOH nanostructures obtained via CBD at various Ga(NO₃)₃ concentrations are shown in Figure 1, where the length, width, and the aspect ratio of at least eight GaOOH nanorods were measured. It was found that the Ga(NO₃)₃ concentration significantly

influenced the synthesis of GaOOH nanorods and the formation of Ga₂O₃ thin films during the annealing process. The GaOOH crystalline quality increased as the Ga(NO₃)₃ concentration increased from 0.025 M (Figure 1a,d) to 0.075 M (Figure 1c,f). The average length, width and the aspect ratio of the GaOOH nanorods prepared from 0.025 M Ga(NO₃)₃ were 0.88 μm , 0.27 μm and 3.23, respectively (Figure 1d). The average length, width and the aspect ratio of the GaOOH nanorods prepared from 0.05 M Ga(NO₃)₃ were 0.92 μm , 0.25 μm and 3.76, respectively (Figure 1e). When the Ga(NO₃)₃ concentration increased to 0.075 M, the average length, width and the aspect ratio of the GaOOH nanorods increased to 1.24 μm , 0.25 μm and 5.06, respectively (Figure 1f). These indicated that the higher concentration of Ga(NO₃)₃ yielded the GaOOH nanorods with better crystallinity.

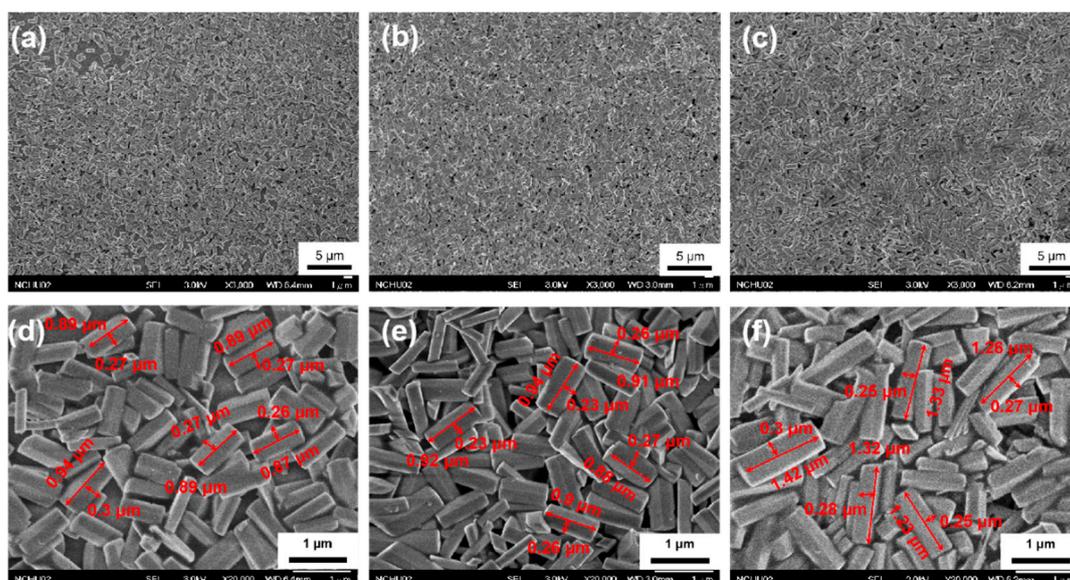


Figure 1. FE-SEM images of GaOOH prepared from Ga(NO₃)₃ at concentrations ranging from 0.025 M to 0.075 M: (a) 0.025 M; (b) 0.05 M; (c) 0.075 M. Their corresponding enlarged micrographs are shown in (d–f), respectively.

Figure 2a shows the XRD pattern of the as-prepared GaOOH obtained at each Ga(NO₃)₃ concentration. The full width at half maximum (FWHM) of each (110) crystal plane diffraction peak was calculated from XRD data as shown in Figure 2b. The XRD patterns indicated the as-prepared GaOOH had an orthorhombic structure (JCPDS no. 01–180). The sharp diffraction peak of the (110) crystal plane appeared at (2θ) 21.4° in the pattern of each sample. This indicated that GaOOH crystal growth proceeded preferentially in the [001] direction at each Ga(NO₃)₃ concentration. The diffraction peaks of the (130), (111), and (240) crystal planes of GaOOH were observed at (2θ) 33.7°, 37.2°, and 54.02°, respectively. The peaks at 21.4° in the patterns of GaOOH nanorods prepared using 0.025 M, 0.05 M, and 0.075 M Ga(NO₃)₃ had FWHMs of 878, 759.7, and 745.1 arcsec, respectively (Figure 2b). The FWHM of this peak was related to the crystallinity of the GaOOH nanorods and indicated that the crystallinity of the nanorods prepared with 0.075 M Ga(NO₃)₃ was higher than that of the other GaOOH samples. The XRD results agreed well with the crystallinity trend of the GaOOH nanorods deposited from various Ga(NO₃)₃ concentrations as presented in Figure 1.

An FTIR spectra of the as-prepared GaOOH nanorods synthesized at each Ga(NO₃)₃ concentration is shown in Figure 3. It is known that the peak at $\sim 3222\text{ cm}^{-1}$ in the FTIR spectra of GaOOH nanorods was assigned to the H-OH stretching vibration, and the stretching vibration of O–H bonds was observed around 1323 cm^{-1} due to the adsorption of water molecules [11,31]. The peak at $\sim 750\text{ cm}^{-1}$ was assigned to the Ga-O-H stretching vibration [20]. It is worthy to mention that the Ga-O-H bond will be enhanced and shifted from ~ 750 to $\sim 820\text{ cm}^{-1}$ as the GaOOH content increased, [31,32]. This confirmed that the GaOOH nanostructure thin films were successfully grown on the glass substrates via CBD.

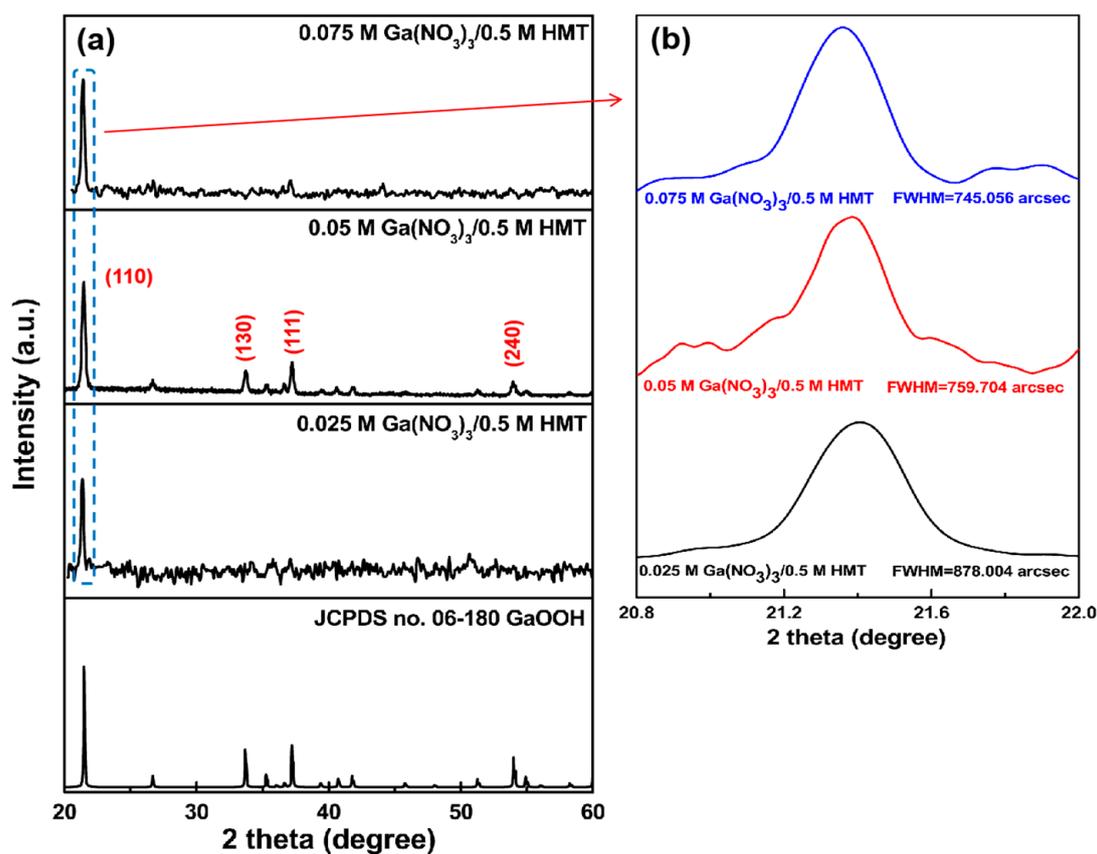


Figure 2. (a) XRD patterns of as-prepared GaOOH nanorods obtained from Ga(NO₃)₃ at concentrations of 0.025 M, 0.05 M, and 0.075 M. (b) FWHMs of the GaOOH (110) crystal plane diffraction peaks shown in (a).

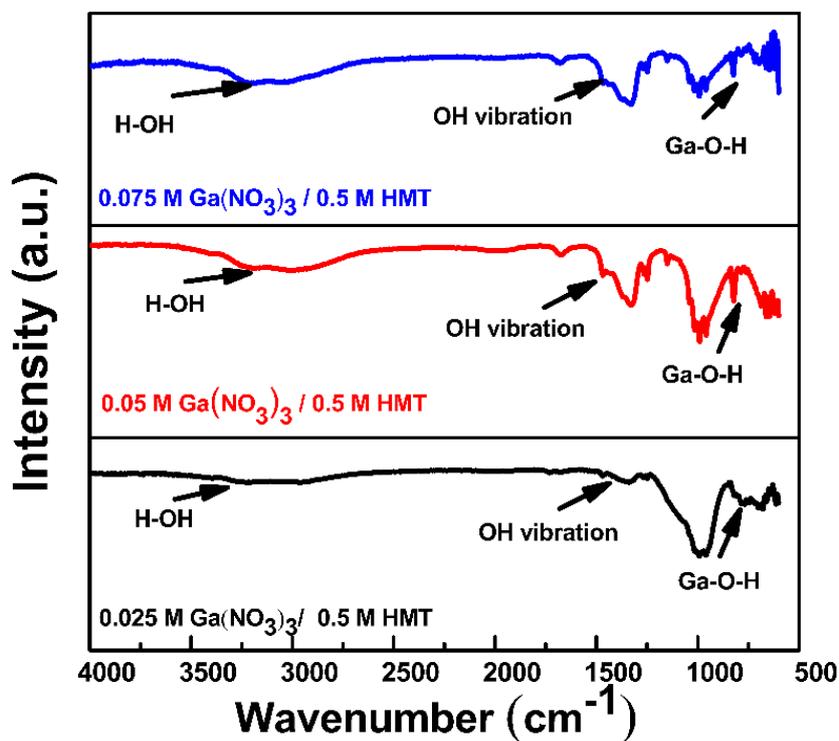


Figure 3. FTIR spectra of GaOOH prepared from Ga(NO₃)₃ at various concentrations.

Figure 4 shows the XRD patterns of Ga₂O₃ in the films after annealing for 3 h at various temperatures from 400 to 600 °C. As shown in Figure 4a, the α-Ga₂O₃ polymorph (JCPDS no. 06–0503) was not indicated in any of the samples annealed at 400 °C. Possibly, the GaOOH could not change to α-Ga₂O₃ at such a low temperature [12]. It was also found that the GaOOH synthesized from 0.025 M Ga(NO₃)₃ did not transform into α-Ga₂O₃ among these annealing temperatures. However, the transformation of as-prepared GaOOH into orthorhombic α-Ga₂O₃ occurred during annealing at 500 and 600 °C. The sharp diffraction peaks of the (104) and (110) α-Ga₂O₃ crystal planes were observed at (2θ) 33.78° and 36.03°, respectively. Table 1 shows the FWHM data of the (104) α-Ga₂O₃ diffraction peaks obtained from 500 and 600 °C-annealed GaOOH samples with 0.05 and 0.075 M Ga(NO₃)₃ concentrations. Obviously, the CBD-GaOOH sample with 0.075 M Ga(NO₃)₃ concentration and post thermal treatment at 500 °C can result in higher crystallinity of α-Ga₂O₃.

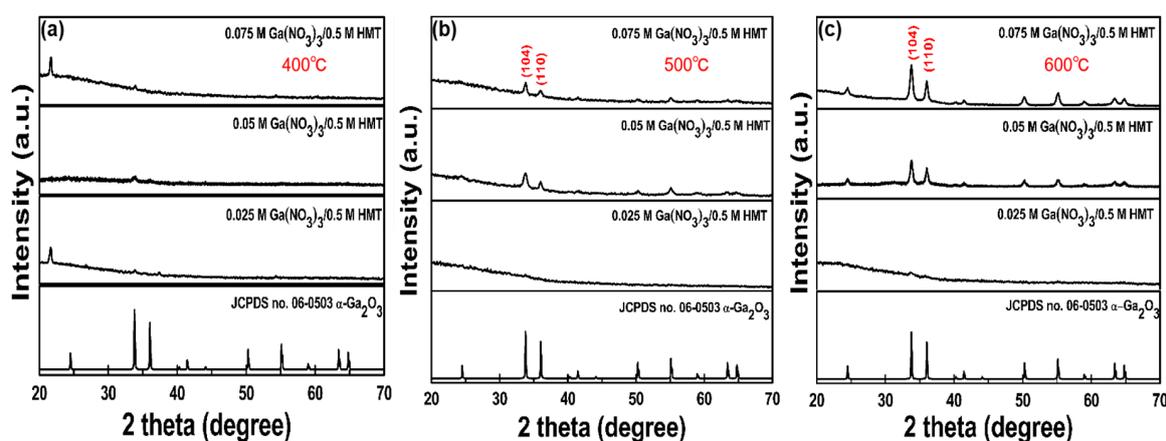


Figure 4. XRD patterns of Ga₂O₃ obtained from thermal-treated GaOOH samples for 3 h at various temperatures (a) 400 °C, (b) 500 °C and (c) 600 °C.

Table 1. The FWHM data of (104) α-Ga₂O₃ diffraction peaks obtained from post-annealed GaOOH samples with 0.05 and 0.075 M Ga(NO₃)₃ concentrations.

Annealed Temperature	0.05 M Ga(NO ₃) ₃	0.075 M Ga(NO ₃) ₃
500 °C	2153.5 arcsec	1567.4 arcsec
600 °C	1715 arcsec	1700.6 arcsec

Figure 5 shows the corresponding FE-SEM micrograph of the α-Ga₂O₃ sample as tabulated in Table 1. After annealing at 500 °C, the average length, width and the aspect ratio of the Ga₂O₃ nanorods obtained from CBD-GaOOH with 0.05 M Ga(NO₃)₃ were 0.94 μm, 0.26 μm and 3.63, respectively (Figure 5a). When the annealing temperature increased to 600 °C, the average length, width and the aspect ratio of the Ga₂O₃ nanorods were 0.89 μm, 0.26 μm, and 3.45, respectively (Figure 5b). Besides, the average length, width and the aspect ratio of the Ga₂O₃ nanorods obtained from 500 °C-annealed GaOOH with 0.075 M Ga(NO₃)₃ were 1.16 μm, 0.23 μm and 5.23, respectively (Figure 5c). When the annealing temperature increased to 600 °C, the average length, width and the aspect ratio of the Ga₂O₃ nanorods were 1.22 μm, 0.26 μm, and 4.68, respectively (Figure 5d). Here, all the data of length, width, and the aspect ratio shown in the micrographs were measured at least eight times. It becomes clear that the higher annealing temperature (i.e., 600 °C) will lead to the slight decrease in the aspect ratio of Ga₂O₃ nanorods. As a result, these nanorods were tightly packed together.

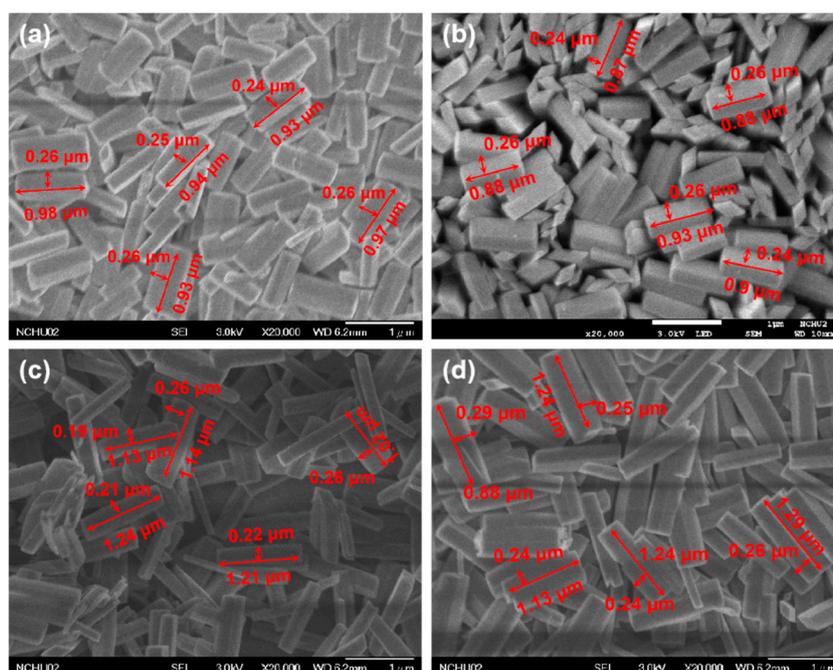


Figure 5. FE-SEM Ga_2O_3 obtained after annealing GaOOH at 500 °C: (a) 0.05 M; (c) 0.075 M; and 600 °C: (b) 0.05 M; (d) 0.075 M.

The elemental compositions of the annealed samples were analyzed via EDS. The EDS spectra of samples prepared using $\text{Ga}(\text{NO}_3)_3$ at various concentrations after annealing at 500 °C are shown in Figure 6. The Si peaks in the EDS spectra were attributed to silicon in the glass substrates. The at.% of Ga in the sample prepared from 0.025 M $\text{Ga}(\text{NO}_3)_3$ was only 1.92% (Figure 6a). When the $\text{Ga}(\text{NO}_3)_3$ concentration increased to 0.05 M, the content of Ga atoms in the sample increased to 16.56% (Figure 6b). Moreover, the at.% of Ga in the sample prepared from 0.075 M $\text{Ga}(\text{NO}_3)_3$ was 30.35% (Figure 6c). From the XRD results as described in Figure 4, the CBD- GaOOH prepared under the lower concentration (0.025 M) cannot be transformed into the $\alpha\text{-Ga}_2\text{O}_3$ regardless of the annealing temperature. It may be due to the fact that the 0.025 M $\text{Ga}(\text{NO}_3)_3$ cannot provide enough Ga content to transform into $\alpha\text{-Ga}_2\text{O}_3$.

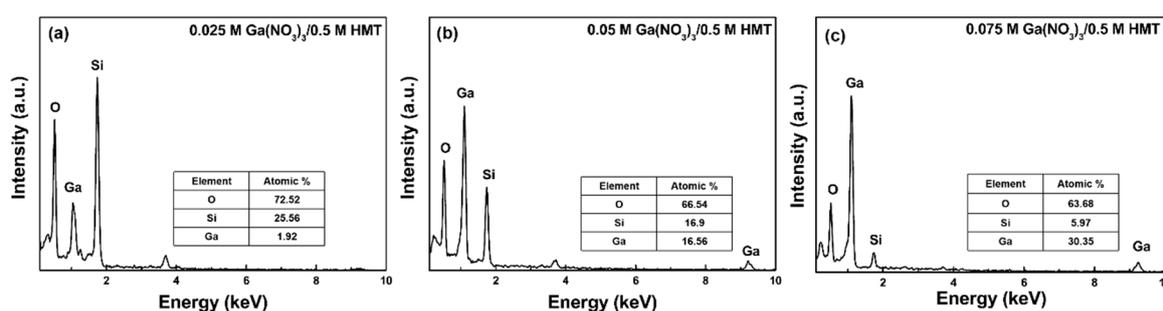


Figure 6. EDS spectra of annealed samples synthesized using (a) 0.025 M $\text{Ga}(\text{NO}_3)_3$, (b) 0.05 M $\text{Ga}(\text{NO}_3)_3$ and (c) 0.075 M $\text{Ga}(\text{NO}_3)_3$. The samples were annealed for 3 h at 500 °C.

The photocatalytic properties of the $\alpha\text{-Ga}_2\text{O}_3$ thin films in the MB solutions were examined under irradiation with UV light. The Ga_2O_3 shows the photocatalytic activity under deep-UV absorption owing to its high bandgap. In general, when the photon was absorbed into photocatalyst, the electron-hole pairs generated on the surface of Ga_2O_3 were used to the degradation of the MB solution. After interacting with aqueous media, these electrons and holes generate hydroxyl ions, which play the significant role in the degradation process. These hydroxyl ions have strong oxidation capabilities as they can mineralize most of organic compounds. Moreover, the photocatalytic activities

intimately depend on the crystallinity and surface area. From the XRD (Figure 4) and FWHMs analyses (Table 1), the good crystallinity of α -Ga₂O₃ sample prepared using 0.075 M Ga(NO₃)₃ can bring the stable photocatalytic properties as compared with those of the other α -Ga₂O₃ samples. The calculated constant reaction rates of MB photodegradation by Ga₂O₃ in the solutions (C/C_0) are plotted as a function of UV irradiation time in Figure 7. C_0 is the initial MB concentration in solution, and C is the MB concentration in the UV-irradiated solution. The rates of MB self-degradation in solutions without the catalyst are shown for comparison. Absorbance by MB was monitored at 664 nm [33]. After 5 h of UV irradiation, 82% of the MB was photodegraded by α -Ga₂O₃ obtained from GaOOH prepared from 0.05 M Ga(NO₃)₃ after annealing at 500 °C (Figure 7b). Photodegradation by α -Ga₂O₃ obtained from the GaOOH sample prepared using 0.075 M Ga(NO₃)₃ after annealing at 500 °C was particularly efficient. After UV irradiation for 5 h, 90% of the MB had been photodegraded by the catalyst (Figure 7c). As shown in Figure 7a, only 29% of the MB was photodegraded by the sample obtained from GaOOH prepared using 0.025 M Ga(NO₃)₃. Based on the XRD results (Figure 4), its low photodegradation efficiency may have been due to the lack of GaOOH transformation into α -Ga₂O₃. The photodegradation efficiencies of α -Ga₂O₃ samples obtained after annealing at 500 °C were higher than those of α -Ga₂O₃ obtained after annealing at 600 °C. This may have been due to the higher the aspect ratio of the α -Ga₂O₃ annealed at 500 °C, which can lead to more surface area under the process of the degradation of the MB solution. The photocatalytic properties of α -Ga₂O₃ observed during the degradation of MB suggested it held promise for environmental remediation applications.

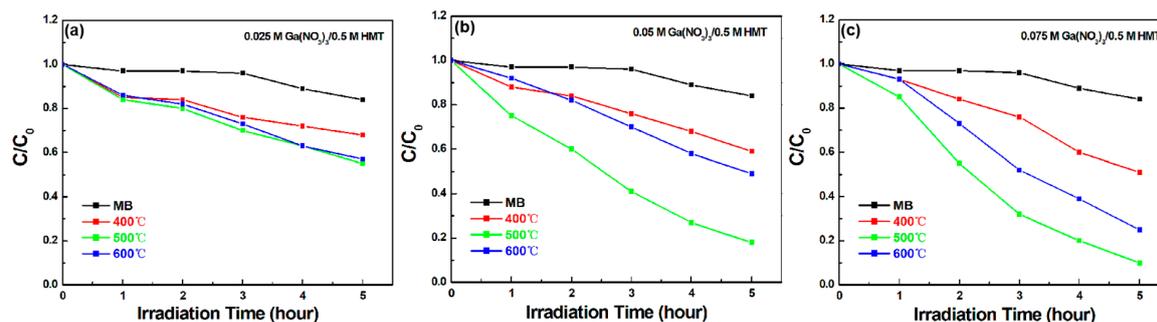


Figure 7. Calculated constant reaction rate of MB photodegradation (C/C_0) by Ga₂O₃ plotted as a function of UV irradiation time. The Ga₂O₃ samples were obtained following annealing of GaOOH prepared at Ga(NO₃)₃ concentrations of (a) 0.025 M, (b) 0.05 M and (c) 0.075 M.

4. Conclusions

GaOOH thin films were successfully grown on glass substrates via CBD at 95 °C. The as-prepared GaOOH thin films were annealed for 3 h at either 400 °C, 500 °C, or 600 °C to convert GaOOH into thin films of α -Ga₂O₃, and the crystal structures and elemental compositions were confirmed through the XRD and EDS analysis, respectively. Nanocrystalline α -Ga₂O₃ films were obtained from GaOOH prepared at Ga(NO₃)₃ concentrations at or above 0.05 M after annealing at 500 °C or 600 °C. The α -Ga₂O₃ sample obtained after annealing GaOOH prepared at a Ga(NO₃)₃ concentration of 0.075 M photodegraded 90% of the MB in a solution irradiated under a UV lamp for 5 h. These results suggest that α -Ga₂O₃ thin films can be very useful alternatives for the photocatalytic degradation of dyes during wastewater treatment.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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