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# Impact of Al doping on a hydrothermally synthesized $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructure for photocatalysis applications

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Aluminum (Al)-doped beta-phase gallium oxide ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>) nanostructures with different Al concentrations (0 to 3.2 at%) are synthesized using a hydrothermal method. The single phase of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is maintained without intermediate phases up to Al 3.2 at% doping. As the Al concentration in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures increases, the optical bandgap of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> increases from 4.69 (Al 0%) to 4.8 (Al 3.2%). The physical, chemical, and optical properties of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures are correlated with photocatalytic activity via the degradation of a methylene blue solution under ultraviolet light (254 nm) irradiation. The photocatalytic activity is enhanced by doping a small amount of substitutional Al atoms (0.6 at%) that presumably create shallow level traps in the band gap. These shallow traps retard the recombination process by separating photogenerated electron-hole pairs. On the other hand, once the Al concentration in the Ga<sub>2</sub>O<sub>3</sub> exceeds 0.6 at%, the crystallographic disorder, oxygen vacancy, and grain boundary-related defects increase as the Al concentration increases. These defect-related energy levels are broadly distributed within the bandgap, which act as carrier recombination centers and thereby degrade the photocatalytic activity. The results of this work provide new opportunities for the synthesis of highly effective  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-based photocatalysts that can generate hydrogen gas and remove harmful volatile organic compounds.

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## Introduction

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) is a wide bandgap semiconductor with five polymorphs designated as  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -phase.<sup>1</sup> Among them,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been widely studied as a promising semiconductor material for power electronics and ultraviolet (UV) photodetectors due to its wide bandgap of  $\sim$ 4.9 eV (ref. 2–4) and its thermodynamic stability.<sup>5</sup>  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is also considered an effective photocatalyst under ultraviolet-C (UVC) light irradiation for the generation of hydrogen<sup>6–8</sup> and removal of volatile organic compounds (VOCs).<sup>9–12</sup>  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has a high redox potential, which is beneficial for photocatalytic reactions under photoexcitation conditions.<sup>9,13</sup> Its redox potential is higher than TiO<sub>2</sub>, so it exhibits better photocatalytic performance than conventional TiO<sub>2</sub> photocatalysts. Meanwhile, the recombination of photogenerated electron-hole pairs is known to severely

degrade photocatalytic efficiency;<sup>14,15</sup> when the electron-hole pairs recombine and the carrier concentrations become depleted, the photocatalytic reactions decrease as a consequence. Indeed, various approaches have been developed to suppress the recombination in Ga<sub>2</sub>O<sub>3</sub>-based photocatalysts.<sup>16–23</sup> Doping in photocatalysts is a method of suppressing the recombination process, which creates available energy states in the bandgap underneath the conduction band edge and/or above the valence band edge.<sup>16–19</sup> These additional energy levels in the forbidden bandgap can separate charged carriers and thereby retard the recombination process, allowing more charged carriers to diffuse in the surface and consequently enhances the photocatalytic reactions.<sup>24,25</sup> Thus far, reports have indicated that dopants in Ga<sub>2</sub>O<sub>3</sub> have reduced the bandgap energy of Ga<sub>2</sub>O<sub>3</sub>, which reduce the benefits of the high redox potential effects that Ga<sub>2</sub>O<sub>3</sub> possesses.<sup>16–20,24–27</sup> Therefore, it would be beneficial to apply a dopant atom that could increase the Ga<sub>2</sub>O<sub>3</sub> bandgap with the dopant concentration. It has been reported that aluminum (Al) can increase the Ga<sub>2</sub>O<sub>3</sub> bandgap upon doping.<sup>28–30</sup> Thus, Al doping in Ga<sub>2</sub>O<sub>3</sub> semiconductors has been intensively studied to modulate the energy bandgap for power electronics and photodetectors.<sup>28–30</sup> However, the photocatalytic properties of Ga<sub>2</sub>O<sub>3</sub> semiconductors have not yet been reported for various Al dopings. In this work, we analyze the effects of Al doping on hydrothermal synthesized  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

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nanostructures for photocatalyst applications. The crystal structures, optical bandgap, and chemical states of the Al-doped  $\text{Ga}_2\text{O}_3$  are investigated with different Al concentrations (0.0 to 3.2 at%), which are also correlated with the photocatalytic activity of Al-doped  $\text{Ga}_2\text{O}_3$ .

## Experimental

### Hydrothermal synthesis of Al-doped $\beta\text{-Ga}_2\text{O}_3$ nanostructures

First, 0.1 M gallium(III) nitrate hydrate ( $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ) was dissolved in 50 mL of deionized (DI) water using a magnetic stirrer at room temperature, where the pH of the initial solution was 2.5. The pH value in the solution was adjusted to approximately 10 by adding an ammonium hydroxide solution ( $\text{NH}_4(\text{OH})$  28 vol% in  $\text{H}_2\text{O}$ ) which was necessary to form  $\beta\text{-Ga}_2\text{O}_3$  nanostructures *via* a hydrothermal reaction.<sup>26,27,31</sup> To dope Al in the  $\beta\text{-Ga}_2\text{O}_3$  nanostructures with different concentrations, different amounts of aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (0.02, 0.064, 0.110, and 0.210 g for Al 0.6, 1.2, 2.2, and 3.2 at% concentrations, respectively) were added into the prepared solution. The pH value of the mixed solution was 10.34 for the intrinsic  $\beta\text{-Ga}_2\text{O}_3$  nanostructures, and the value continued to decrease as the Al concentration increased, ultimately reaching 10.08 for the Al 3.2 at. % -doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures. This pH value reduction was caused by the aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) in the mixed solution. The supersaturated mixed solution was transferred to a Teflon-lined stainless-steel autoclave, thermally treated at 140 °C for 10 h, and subsequently cooled down naturally to room temperature.<sup>26,27,31</sup> After the hydrothermal synthesis process,  $\alpha\text{-GaOOH}$  nanostructures with different Al concentration were collected, washed three times with DI water, and then dried in an oven at 70 °C for 6 h. It is noted that  $\alpha\text{-GaOOH}$  nanostructures were precipitated in dissolved solutions ( $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ) with an ( $\text{NH}_4(\text{OH})$ ) alkali in this work, and it was reported that the  $\alpha\text{-GaOOH}$  nanostructures were also precipitated in dissolved solutions ( $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ) with other alkalis such as  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NaHCO}_3$ , and  $\text{Na}_2\text{CO}_3$ .<sup>32</sup> In addition, the morphologies of the  $\text{GaOOH}$  were found to have significantly different in terms of pH values.<sup>33</sup> Finally, Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures were obtained after annealing the Al-doped  $\text{GaOOH}$  nanostructures in an  $\text{O}_2$  ambient at 1000 °C for 6 h. After each experiment set, approximately 500 mg of  $\text{GaOOH}$  was obtained with different Al concentrations. This was converted into about 450 mg of  $\beta\text{-Ga}_2\text{O}_3$ .

### Characterization of Al-doped $\beta\text{-Ga}_2\text{O}_3$ nanostructures

The crystal structures and morphologies of the samples were characterized using a powder X-ray diffraction system (XRD, Rigaku SmartLAB, Tokyo, Japan) over the  $2\theta$  range with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm) and using a field-emission scanning electron microscope (FESEM, JSM-7100F, JEOL, Peabody, MA, USA), respectively. The specific surface areas of the samples were measured *via* the Brunauer–Emmett–Teller (BET) method using a conventional flow apparatus (BELSORP-mini II, Osaka, Japan) with nitrogen adsorption at  $-196$  °C. The chemical states

of the elements presented on the sample surface were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, K-ALPHA+ System), which also determined the Al concentrations in the  $\beta\text{-Ga}_2\text{O}_3$  nanostructures. The optical bandgaps of the samples were extracted using diffuse reflectance spectroscopy (DRS, SHIMADZU, SolidSpec-3700) *via* Tauc plots (direct bandgap model). Relative redox potential of the Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures was obtained from the optical bandgaps. The crystalline domain sizes of the Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures were subsequently estimated using the Scherrer equation<sup>34</sup> in eqn (1), which is inversely proportional to the total length of the grain boundaries (GBs).

$$\text{Domain size} = \frac{K\lambda}{\beta_{\text{size}} \cos \theta} \quad (1)$$

where K is a dimensionless shape factor of 0.9,  $\lambda$  is an X-ray wavelength of 0.15405 nm,  $\beta_{\text{size}}$  is the full width at half maximum (FWHM) of the XRD peaks, and  $\theta$  is the Bragg angle.

### Photocatalytic activity of Al-doped $\beta\text{-Ga}_2\text{O}_3$ nanostructures

The photocatalytic activity of the samples was evaluated *via* the degradation of a methylene blue (MB) solution, which is a model system. It was found that the MB oxidation is mainly driven by the OH radical that is generated due to the photocatalytic activity.<sup>35</sup> 4 mg of each sample was homogeneously dispersed in the 4 mL MB solution ( $1.56 \text{ mg L}^{-1}$  in DI water), which was then exposed to the 6 W ultraviolet-C (UVC) lamp (UVG-11, Germany) with a wavelength center at 254 nm and  $312 \mu\text{W cm}^{-2}$  for 10 min. After the  $\beta\text{-Ga}_2\text{O}_3$  nanostructures were filtered through a syringe filter ( $0.45 \mu\text{m}$ ), the absorbance of the MB solution was measured using UV-VIS spectrophotometers (UV-3600 plus, Shimadzu, Kyoto, Japan). An intact MB solution (without UVC exposure) was used as a control for comparison. The photocatalytic activity (%) of the Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures with different Al concentrations was defined using eqn (2).

$$\text{Photocatalytic activity} = \frac{C_i - C}{C_i}, \quad (2)$$

where  $C_i$  and  $C$  are the absorbances at  $\lambda = 664$  nm from the intact MB solution and the UVC-exposed MB solution in the presence of Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures with different Al concentrations, respectively. The photogenerated electron–hole pairs in the Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures in the MB solution generated reactive oxygen species that eventually decomposed the MB.<sup>36</sup>

Redox potential (RP), surface area (SA), and oxygen deficiency defects (OD) were defined based on the extracted optical bandgap, the specific surface area value obtained through the BET analysis method, and O 1s spectra using XPS, respectively. Crystallographic defects (CD) and grain boundary-induced defects (GD) were respectively defined based on the average values of the intensity and domain size of the three ( $-401$ ), ( $002$ ), and ( $111$ ) peaks obtained through XRD analysis.

## Results and discussion

The X-ray diffraction patterns of the  $\text{GaOOH}$  and Al-doped  $\text{Ga}_2\text{O}_3$  nanostructures are presented in Fig. 1(a). The intrinsic



Ga<sub>2</sub>O<sub>3</sub> nanostructures were indexed to the monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The single phase was maintained without intermediate phases up to Al 3.2 at%, which was in agreement with previous results in which the maximum solid solubility of Al in the Ga<sub>2</sub>O<sub>3</sub> was 80 at%.<sup>37</sup> The crystal structure and domain size of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were affected by the amounts of Al dopant, as shown in Fig. 1(b–d). In Fig. 1(b) and (c), the peak intensities of ( $\bar{4}01$ ), (002), and (111) decrease, and the peak positions shift toward a higher  $2\theta$  angle as the Al concentration increases. These results indicate that the Al dopants in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures reduce the crystallinity degree and lattice constant of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures, resulting in a maximum compressive strain as high as approximately 0.35% at the Al concentration of 3.2 at%. The 8% smaller radius of the Al<sup>3+</sup> (57 ppm), which was substituted at the octahedral sites in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,<sup>38</sup> than that of the Ga<sup>3+</sup> (62 ppm) caused these structural changes.<sup>39</sup> In addition, as seen in Fig. 1(c), the compressive strain of the Al-doped Ga<sub>2</sub>O<sub>3</sub> nanostructures was compared to that of the thin film  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with the same Al concentration.<sup>29</sup> The results revealed that substitutional Al doping in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanomaterials induced a higher compressive strain than in the thin film, presumably due to the higher surface energy in the nanomaterials. Fig. 1(d) shows the average domain sizes of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with Al doping concentrations, showing that the normalized domain size decreased

down to 65% at the Al concentration of 3.2 at%. The decrease of the domain size with the Al doping concentration was related to the lattice mismatch in the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures. The crystallographic defects and/or disorders presumably enhanced the nucleation site density during the crystallization process, reducing the domain size. In addition, the Al dopants in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures were able to affect the crystal growth of certain crystal faces, affecting the nanostructure shape and size. The normalized intensity and domain size in Fig. 1(b and d) are inversely proportional to the crystallographic and GBs-induced defects, respectively. Those defects were able to generate additional deep level states in the bandgap that could act as recombination centers of the charged carriers,<sup>40</sup> which will be correlated with the photocatalytic activity in Fig. 6 and 7.

The SEM images of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with Al concentrations are presented in Fig. 2(a–e). The intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures presented a spindle-like morphology with an average length of 1.25  $\mu$ m. This morphology, often observed in hydrothermal synthesized Ga<sub>2</sub>O<sub>3</sub> nanostructures,<sup>41,42</sup> morphed into nanorod structures with an average length of 0.8  $\mu$ m at the Al concentration of 3.2 at%, as shown in Fig. 2(a–e). The pH value of the precursor solution for the intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures was initially 10.34 and gradually decreased, as summarized in Fig. 2(f). The reduction

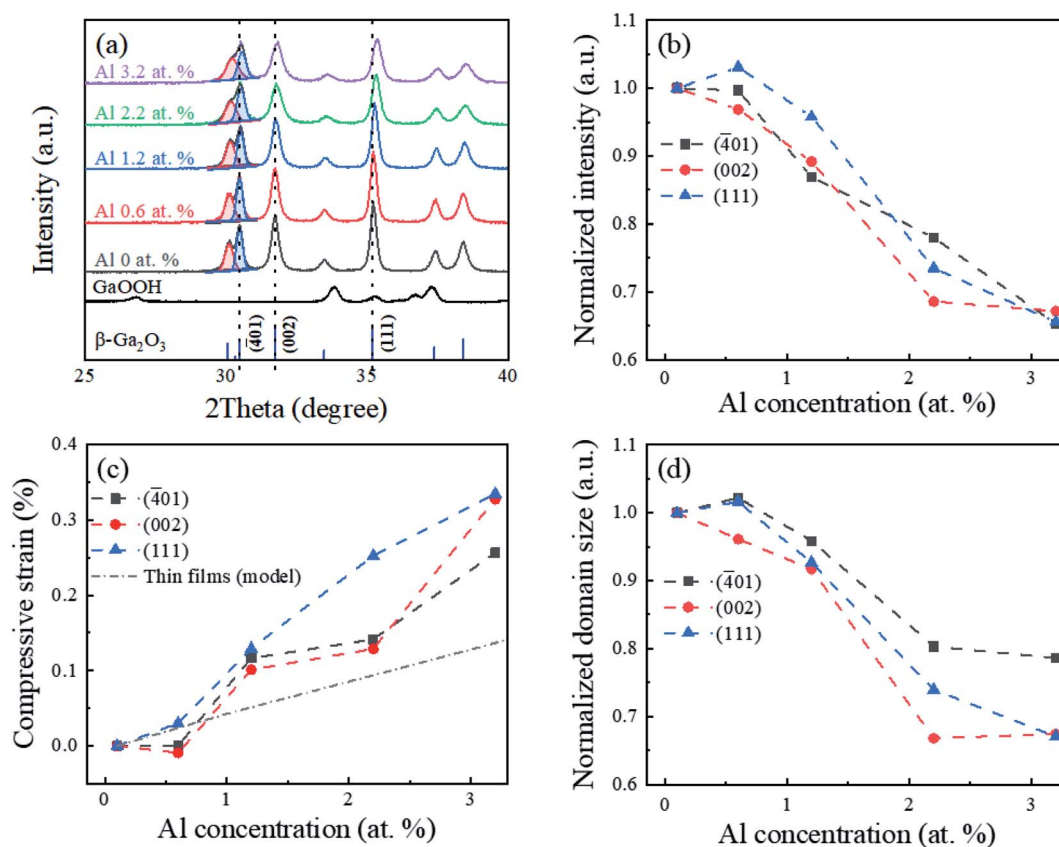


Fig. 1 (a) XRD patterns of GaOOH and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with different Al concentrations; the bottom ticks indicate PDF Card No. 01-076-0573 for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. (b) Normalized peak intensity, (c) compressive strain, and (d) normalized domain size of ( $\bar{4}01$ ), (002), and (111) planes as a function of Al concentrations. The compressive strain in this work was compared with that of the thin film (model).<sup>29</sup>

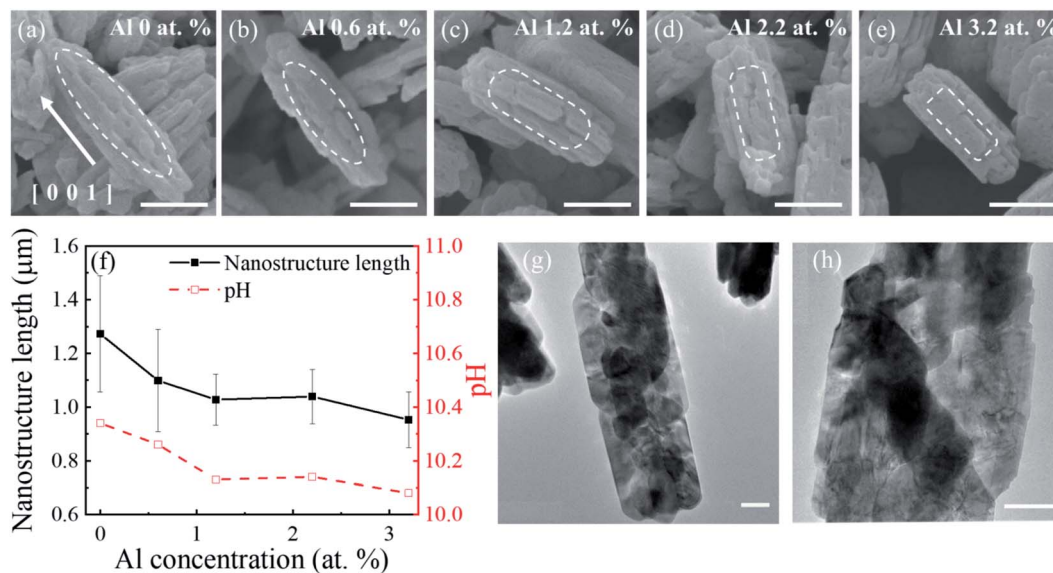


Fig. 2 (a–e) SEM images (scale bar: 500 nm) and (f) average length of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with increasing Al concentrations. TEM images (scale bar: 100 nm) of (g) GaOOH nanostructures (before annealing) and (h)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures (after annealing) without Al doping.

of the pH in the precursor solution with the Al concentration was believed to have changed the spindle-like morphology to the nanorod structures and reduce the length as well. These results were consistent with those in previous studies.<sup>42</sup> This implied that the Al atoms in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures and/or pH variation in the mixed solution were involved in the nucleation growth during the hydrothermal process. Fig. 2(g and h) show TEM images of the synthesized GaOOH (before annealing) and the corresponding  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> of the spindle-like morphology (after annealing) without Al dopants, respectively. The synthesized GaOOH of the orthorhombic structure consisted of well-stacked nanoplates, which transformed into the rough-surface monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> after Ostwald's ripening (annealing).<sup>43</sup>

The specific surface area of the Al-doped Ga<sub>2</sub>O<sub>3</sub> nanostructures was investigated using the BET method, as shown in Fig. 3. In Fig. 3(b), the surface area remains almost unchanged

at around  $7.4\text{--}7.6\text{ m}^2\text{ g}^{-1}$  within the Al range of 0–1.2 at.%, and then increases with the Al concentrations. The increase of the specific surface area at the higher Al concentrations could be explained with the morphology change from the spindle-like morphology to the microrod structure along with the length reduction, as shown in Fig. 2. Higher specific surface areas are beneficial for photocatalytic reactions because the redox reactions occur on the photocatalyst surface, which would be correlated with the photocatalytic activity in Fig. 6.

The core-level spectra of the Ga 2p, Al 2p, and O 1s orbitals of the intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures are compared with those of Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures for the different Al concentrations in Fig. 4. The binding energy (BE) of the Ga<sup>3+</sup> (Ga<sub>2</sub>O<sub>3</sub>) 2p<sub>3/2</sub> peaks in the intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures was 1117.4 eV in Fig. 3(a), which was attributed to Ga–O bonding. The additional peak at 1119.1 eV was observed and its intensity

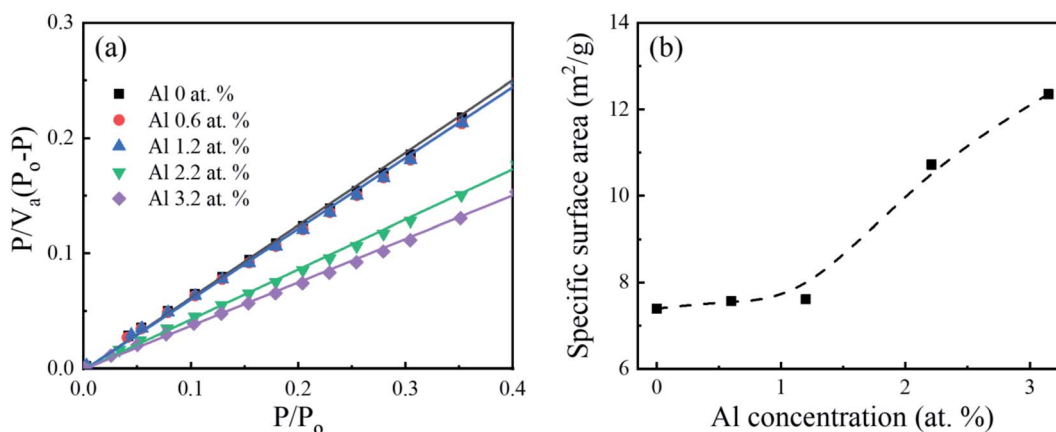


Fig. 3 (a) BET surface area plot for Al-doped Ga<sub>2</sub>O<sub>3</sub> nanostructures with different Al concentrations and (b) specific surface area as a function of Al concentrations;  $V_a$ ,  $P_o$ ,  $P$ , and  $P/P_o$  are the adsorbed gas quantity, saturation pressure of the adsorbate, equilibrium pressure of the adsorbate, and relative pressure, respectively.



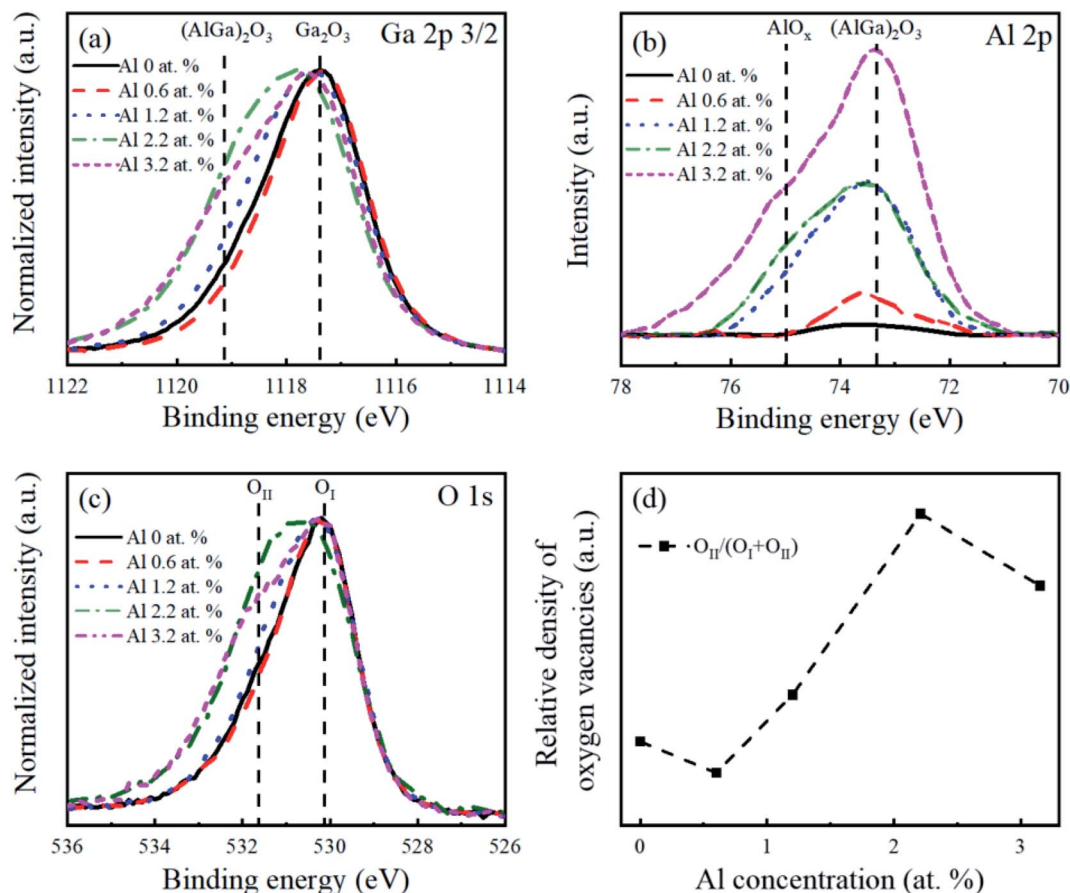


Fig. 4 XPS analysis of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with different Al concentrations: core-level spectra of (a) Ga 2p<sub>3/2</sub>, (b) Al 2p, and (c) O 1s. The XPS intensity in (a and c) is normalized to increase clarity. (d) Relative intensity of O<sub>II</sub>/(O<sub>I</sub> + O<sub>II</sub>) in O 1s spectra as a function of Al concentrations. The peak energies were calibrated using an adventitious C 1s of 284.68 eV.

increased with the Al concentration. The peak at 1119.1 eV was assigned to (AlGa)<sub>2</sub>O<sub>3</sub> because it was higher than the G–O peak, as with the previous result.<sup>44</sup> The intensity of the Al 2p peak increased as the Al concentration increased, as shown in Fig. 4(b). The Al 2p peak for the 0.6 at% Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures was located at 73.3 eV, indicating the formation of (AlGa)<sub>2</sub>O<sub>3</sub>. As the Al concentration increased, the additional peak at 75 eV appeared, which was considered to be Al–O bonds.<sup>30,45,46</sup> This Al–O peak shifted toward the higher binding energy with the Al concentration in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which was also in good agreement with previous reports.<sup>30,46,47</sup> The presence of Al–O bonding in the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures presumably originated from the hydrothermal solution because the formation of [Al(OH)<sub>2</sub> aq<sup>+</sup>] and [AlO<sub>2</sub> aq<sup>−</sup>] was thermodynamically favorable; the Gibbs free energies of the [Al(OH)<sub>2</sub> aq<sup>+</sup>] and [AlO<sub>2</sub> aq<sup>−</sup>] were calculated as −914.2 and −830.9 kJ mol<sup>−1</sup>, respectively.<sup>47</sup> In Fig. 4(c), two O 1s peaks located at 530.2 eV (O<sub>I</sub>) and 532.0 eV (O<sub>II</sub>) represented the O<sub>2</sub><sup>−</sup> ions in the oxygen-saturated and oxygen-deficient regions, respectively.<sup>48</sup> The density of the oxygen vacancies represented by the intensity ratio of O<sub>II</sub>/(O<sub>I</sub> + O<sub>II</sub>) is plotted in Fig. 4(d). This indicates that the small amount of Al doping (0.6 Al at%) reduced the number of oxygen-deficient defects in the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures. Meanwhile, the defect density tended to increase

with Al concentration when the Al concentration exceeded 0.6 at% in Fig. 4(d). This indicated that the low Al concentration (0.6 at%) in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures healed the oxygen defects rather than generate additional oxygen defects.

Fig. 5(a) shows the optical absorbance and Tauc plots (direct bandgap model) of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with different Al concentrations. The optical bandgaps of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures were obtained using a linear extrapolation from their Tauc plots and compared with those of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin films, as shown in Fig. 5(b). The extracted optical bandgap energy of the intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures was ~4.69 eV, and the bandgap energy increased with the Al concentration. This increase in the bandgap with the Al concentration was mainly caused by the increase in the conduction band edge compared with the changes in the valence band edge.<sup>28–30</sup> The redox potential (reduction ability) could be enhanced with the increase in the Al concentration and consequently improve the photocatalytic activity of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The nanostructure bandgap was smaller than that of the thin films by around 0.2 eV, which was attributed to the light scattering effect in the nanostructures.<sup>49</sup>

Fig. 6(a and b) show the absorbance spectra of the MB solutions and corresponding photocatalytic activity of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures as a function of Al concentration,



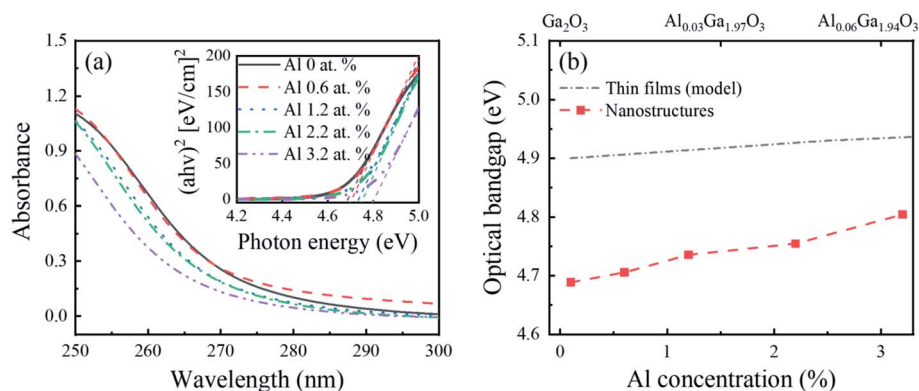


Fig. 5 (a) Optical absorbance spectra and Tauc plots (direct bandgap model) and (b) corresponding optical bandgap of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures with different Al concentrations;  $\alpha$  is the absorption coefficient,  $h$  is the Planck constant, and  $\nu$  is the frequency of the electromagnetic radiation. The optical bandgap of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures is compared with that of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin films.<sup>29</sup>

respectively. The photocatalytic activity of the intrinsic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures was  $\sim 62\%$ , and this value increased significantly up to  $88\%$  with the Al (0.6 at. %) doping in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures. However, when the Al concentration further increased within the Al range of 0.6–3.2 at. %, the photocatalytic activity decreased. It is noted that this degradation of MB solution was not affected by the pH value in the range of 8.0 to 10.5.<sup>50</sup> Fig. 6(b) also shows the Al dopant effect on the redox potential, surface area, crystallographic defects, oxygen defects, and GB-induced defects, and their correlation with the photocatalytic activity. The redox potential and surface area increased as the Al concentration increased in Fig. 6(b). Although photocatalytic activity was expected to enhance as the redox potential<sup>51–53</sup> and surface area<sup>9,13</sup> increased, the photocatalytic activity continued to decrease with Al concentration (0.6 to 3.2 at. %) in this work. It indicated that apart from the redox potential and surface area, other factors dominated the photocatalytic activity of the Al-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures. Meanwhile, defects in the photocatalysts can either enhance or degrade the photocatalytic activity by acting as carrier separation and recombination sites, respectively.<sup>54–56</sup> Fig. 6(b) shows that as the Al

concentration increased (0.6 to 3.2 at. %), the crystallographic, oxygen, and GB-related defects continued to increase but accordingly the photocatalytic activity continued to decrease. The results indicated that the substituted Al atoms in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures generated the crystallographic, oxygen, and GB-related defects that acted as charge recombination sites and degraded the photocatalytic activity consequently. However, this could not explain the significant enhancement of photocatalytic activity with the small amount of Al (0.6 at. %) doping in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures. We presumed that the amount of Al concentration is important factor for photocatalytic activity and hypothesized that when the small amount of Al atoms (0.6 at. %) was doped in the Ga<sub>2</sub>O<sub>3</sub>, the shallow trap sites were introduced to the forbidden bands due to the dopant-induced oxygen vacancy, as shown in Fig. 7(a). These defects could retard the recombination process by separating the photogenerated electron–hole pairs, which thereby enhanced the photocatalytic activity. On the other hand, once the Al concentration in the Ga<sub>2</sub>O<sub>3</sub> exceeded 0.6 at. %, the crystallographic disorder, oxygen vacancy, and GB-related defects increased as the Al concentration increased. These defect-

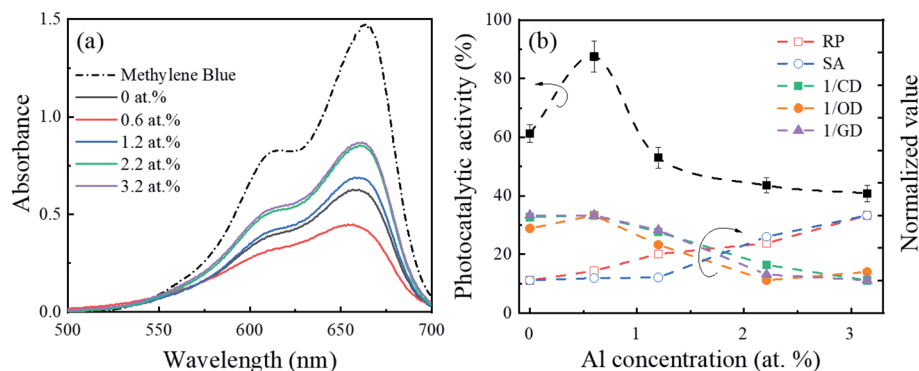


Fig. 6 (a) Absorbance spectra of the MB solution and (b) photocatalytic activity of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanostructures as a function of Al concentration under UVC irradiation for 10 min at room temperature. The error bars in the photocatalytic performance are graphical representations of a standard deviation of triple measurements. The photocatalytic activity is correlated with different parameters affecting the photocatalytic reactions, which are normalized, and the sensitivity factor is not considered; RP, SA, CD, OD, and GD represent the redox potential (Fig. 5(b)), surface area (Fig. 3(b)), crystallographic defects (Fig. 1(b)), oxygen defects (Fig. 4(d)), and GB-induced defects (Fig. 1(d)), respectively.

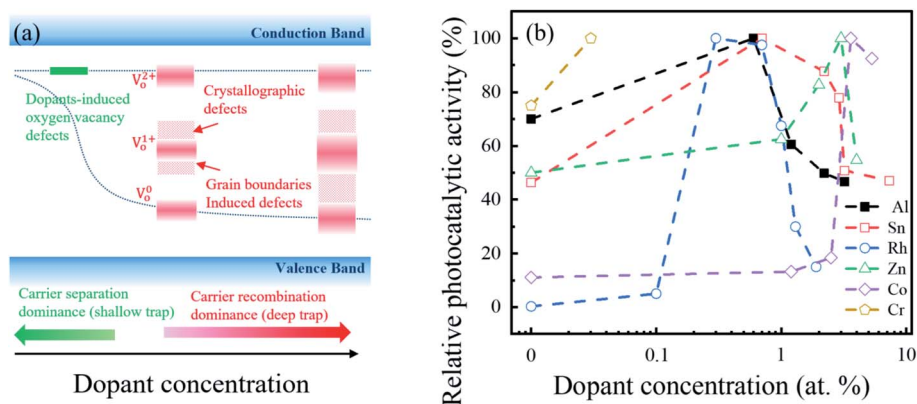


Fig. 7 (a) Trap site distribution as a function dopant concentration. The deep trap levels are generated due to the GB/crystallography<sup>57,58,60</sup> and oxygen vacancy<sup>59</sup> defects. (b) Benchmark of relative photocatalytic activity of  $\text{Ga}_2\text{O}_3$  with different dopants and concentrations; Al and Sn via MB degradation under 254 nm,<sup>26</sup> Cr via Rhodamine B (RhB) degradation under 254 nm,<sup>17</sup> Co via Congo red (CR) degradation under 254 nm,<sup>61</sup> Zn via gas conversion under 254 nm,<sup>18</sup> and Rh via  $\text{CO}_2$  conversion under 300 nm.<sup>16</sup>

related energy levels could be broadly distributed within the bandgap, as shown in Fig. 7(a), and acted as carrier recombination centers,<sup>57–59</sup> which degraded the photocatalytic activity.

Fig. 7(b) shows the relative photocatalytic activities of the  $\beta\text{-Ga}_2\text{O}_3$  nanostructure for different doping materials and concentrations.<sup>16–18,26,57–61</sup> This comparison revealed that the photocatalytic performance of the given  $\text{Ga}_2\text{O}_3$ -based photocatalyst increased at certain small amounts of dopants, but decreased with large amounts of dopants. Therefore, an optimal balance between charge separation and recombination *via* doping approaches is important for  $\text{Ga}_2\text{O}_3$ -based photocatalyst.

## Conclusion

The photocatalytic activity of Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures was investigated at different Al concentrations within the Al range of 0–3.2 at%. The single phase of the  $\beta\text{-Ga}_2\text{O}_3$  was maintained without intermediate phases up to Al 3.2 at% doping. As the Al concentration in the  $\beta\text{-Ga}_2\text{O}_3$  nanostructures increased, the optical bandgap energy of the Al-doped  $\beta\text{-Ga}_2\text{O}_3$  nanostructures increased. With a small amount of substitutional Al (0.6 at%) doping in the  $\beta\text{-Ga}_2\text{O}_3$  nanostructures, the degree of crystallinity, compressive strain, domain size, surface area, and oxygen defects remained unchanged, but they significantly changed as the Al concentration further increased beyond 0.6 at%. The photocatalytic activity was enhanced by doping a small amount of substitutional Al atoms (0.6 at%), which was attributed to the presence of the shallow trap level in the band gap. These shallow-level defects retarded the recombination process by separating photogenerated electron-hole pairs and thereby enhanced the photocatalytic activity. On the other hand, once the Al concentration in the  $\text{Ga}_2\text{O}_3$  exceeded 0.6 at%, the crystallographic disorder, oxygen vacancy, and GB-related defects increased as the Al concentration increased. These defect-related energy levels could be broadly distributed within the bandgap, which acted as carrier recombination centers and consequently degraded the photocatalytic activity. The photocatalytic activity of the Al-doped  $\beta\text{-Ga}_2\text{O}_3$

nanostructures was strongly correlated with the recombination process rather than the surface area and redox potential. To further enhance the photocatalytic activity of  $\text{Ga}_2\text{O}_3$ -based nanostructures, a small amount of doping without causing noticeable crystal and oxygen defects is recommended.

## Conflicts of interest

There are no conflicts to declare.

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