

Cite this: *RSC Adv.*, 2018, 8, 14328

## Photocatalytic degradation of ethylene by Ga<sub>2</sub>O<sub>3</sub> polymorphs

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In this work, we fabricated four different Ga<sub>2</sub>O<sub>3</sub> polymorphs, namely,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, and investigated their photocatalytic activities by the degradation of ethylene under ultraviolet (UV) light irradiation. Owing to the more positive valence band, all these Ga<sub>2</sub>O<sub>3</sub> polymorphs are more photocatalytic reactive than P25 during the degradation of ethylene. The normalized photocatalytic ethylene degradation rate constants of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs follow the order:  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> >  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, which is mainly determined by the position of VBM and the crystallinity of the samples. Among these Ga<sub>2</sub>O<sub>3</sub> polymorphs,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, with the highest surface area, exhibits the highest activity during photocatalytic ethylene degradation, and the degradation rate constant is almost 10 times as that of P25. Furthermore, with the most positive CBM,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> produces the least CO. These attributes are beneficial for ethylene degradation during post-harvest storage of fruits and vegetables, which makes  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> a potential candidate for practical photocatalytic ethylene degradations.

Received 13th March 2018

Accepted 5th April 2018

DOI: 10.1039/c8ra02212g

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### 1. Introduction

Ethylene is a colorless and odorless gas that can be produced naturally by plant tissues and biomass fermentation. As ethylene can greatly accelerate the ripening process of fruits and vegetables, serious problems would be encountered during the postharvest storage of fruits and vegetables such as over-ripening, senescence, stimulated chlorophyll loss or promoted abscission of leaves and flowers, *etc.*<sup>1,2</sup> Therefore, it is important to prevent the ethylene action during postharvest storage of fruits and vegetables. Up to now, various methods have been developed to control the action of ethylene such as the use of strong oxidizing agents to decompose ethylene, employing carbon or zeolites as ethylene absorber, or the use of ethylene inhibitor to prevent the synthesis of ethylene, *etc.*<sup>3–7</sup> However, these techniques are usually expensive and require either long exposure times or complicated systems.

Photocatalysis is a potential technique that can utilize solar energy to decompose organic pollutants or generate H<sub>2</sub> by water splitting. Recently, it also emerges as a promising route to prevent ethylene action during the postharvest storage of fruit and vegetables owing to its low cost and continuity.<sup>8–12</sup> For example, Amodio *et al.* demonstrated the completely elimination of ethylene (100 ppm) over TiO<sub>2</sub>/SiO<sub>2</sub> composites under UV light irradiation for 2 h. However, comparing to traditional technique, *i.e.*, potassium permanganate based formulation,

the photocatalytic degradation rate is still lower.<sup>11</sup> Therefore, it is still needed to further improve the photocatalytic ethylene degradation activity for practical applications.

Up to now, most studies on photocatalytic ethylene degradations are mainly based on the use of TiO<sub>2</sub> as photocatalyst. As the photocatalytic activity on decomposing organic pollutants are mainly determined by the position of the conduction and valence bands of semiconductors, photocatalysts with wider band gaps, such as Ga<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, are expected to be more efficient than TiO<sub>2</sub>. Among these wide band gap semiconductors, Ga<sub>2</sub>O<sub>3</sub> is regarded as one of the most promising semiconductors owing to its superior physical and chemical properties and a wide band gap 4.2–5.0 eV, which has been widely investigated on overall water splitting, benzene decomposition and CO<sub>2</sub> reduction, *etc.*<sup>13–17</sup> Therefore, Ga<sub>2</sub>O<sub>3</sub> is expected to be more efficient than TiO<sub>2</sub> on photocatalytic ethylene degradations. Moreover, Ga<sub>2</sub>O<sub>3</sub> has four polymorphs, namely,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub>, which could lead to the variations on photocatalytic activities. For example, Hou *et al.* systematically investigated the photocatalytic activity of Ga<sub>2</sub>O<sub>3</sub> polymorphs by decomposing volatile organic compounds, *i.e.*, benzene, toluene, and ethylbenzene. And  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is found to be the most efficient among the Ga<sub>2</sub>O<sub>3</sub> polymorphs, which is more than 3 times higher than that of TiO<sub>2</sub>.<sup>18</sup> However, the investigations on the photocatalytic ethylene degradations over Ga<sub>2</sub>O<sub>3</sub> polymorphs have not been systematically investigated yet.

In this work, we fabricated four Ga<sub>2</sub>O<sub>3</sub> polymorphs, namely,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, and investigated their photocatalytic activities on ethylene degradation. The normalized photocatalytic degradation rate constant of the as-prepared Ga<sub>2</sub>O<sub>3</sub>

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polymorphs is found to follow the order of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> >  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, which is mainly determined by the position of VBM and the crystallinity of the samples. Owing to the highest surface area,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> exhibits the highest apparent photocatalytic activity on oxidizing ethylene to CO<sub>2</sub>, which makes it a potential candidate for practical photocatalytic ethylene degradations.

## 2. Experimental details

### 2.1 The fabrication of Ga<sub>2</sub>O<sub>3</sub> polymorphs

The Ga<sub>2</sub>O<sub>3</sub> polymorphs were fabricated by following the procedures reported elsewhere.<sup>19–21</sup>  $\alpha$ - and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were prepared by calcining GaO(OH) precursors at different temperatures according to literature.<sup>19</sup> In details, 3 g of gallium nitrate hydrate was firstly dissolved in 40 ml ethanol (50 vol%). And then, the solution was slowly added into the aqueous ammonia with the same volume with continuous stirring. After stirring for 1 h at room temperature, the precipitates were filtered and washed with ethanol and deionized water, which was subsequently dried at 60 °C overnight.  $\alpha$ - and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were obtained by calcining the above precursors at 400 and 800 °C for 4 h, respectively.  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> was prepared as follows: 3 g nitrate hydrate was dissolved in 50 ml ethanol solvents, concentrated aqueous ammonia diluted in ethanol (50 vol%) was slowly

added under continuous stirring at room temperature until no further precipitate was observed to form. The resulting gel was filtered, thoroughly washed with distilled and ethanol, and vacuum-dried in a desiccator. After that, the metal oxide obtained after it was calcined at 500 °C for 1 hour.<sup>20,21</sup>  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> was prepared by directly calcining gallium nitrate hydrate at 320 °C for 12 hours as reported.<sup>22</sup>

### 2.2 Characterizations

The XRD patterns of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs were characterized on a Bruker D8 advanced X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The morphologies of the Ga<sub>2</sub>O<sub>3</sub> polymorphs were obtained by scanning electron microscopy (SEM, Hitachi S-4800), and high-resolution electron transmission electron microscopy (HR-TEM, JEM 2100). The BET surface areas were determined by using N<sub>2</sub> adsorption/desorption isotherm measurements by a Micromeritics ASAP 2020 apparatus. The UV-vis diffuse reflectance spectroscopy (DRS) measurements were recorded on a Shimadzu UV 2550 spectrophotometer equipped with an integrating sphere. X-ray photoelectron spectroscopy (XPS) valence band spectra were measured in a VG Micro-Tech ESCA 3000 X-ray photoelectron spectroscope within monochromatic Al K $\alpha$  radiation, the photo energy is 1486.6 eV at the condition of  $>1 \times 10^{-9}$  torr.

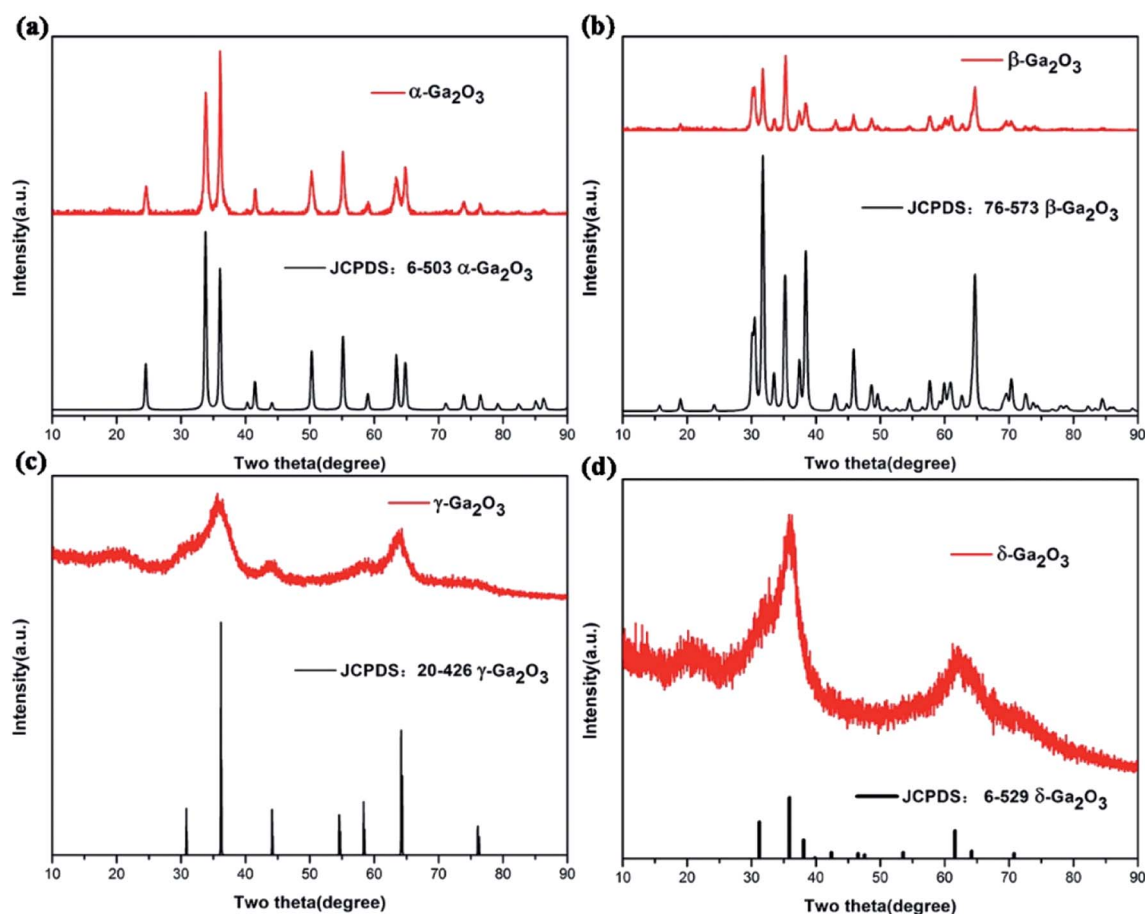


Fig. 1 The XRD patterns of as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs: (a)  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, (b)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, (c)  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, (d)  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, respectively.



### 2.3 Photocatalytic experiments

The photocatalytic experiments were performed in a closed quartz reactor with a total volume of 420 ml under UV light irradiation (UV lamp, 30 W, 185 nm and 254 nm). Firstly, 0.3 g as-prepared  $\text{Ga}_2\text{O}_3$  polymorph samples were spread uniformly at the bottom of the reactor. Then, 0.5 ml  $\text{C}_2\text{H}_4$  was injected into the sealed quartz reactor by a micro-syringe. The quartz reactor was subsequently kept in dark under magnetic stirring for 2 h to reach adsorption–desorption equilibrium before turning on the UV lamp. The reaction temperature was kept at 5 °C by water cooling during the whole experiment. The humidity in the photocatalytic process was 10%. Finally, the quartz reactor was exposed to UV light irradiation for photocatalytic reactions. 30  $\mu\text{l}$  gas was withdrawn from the reactor at 1 h intervals to analyze the concentration of ethylene and carbon dioxide by injection into a gas chromatograph (Shimadzu GC-2014C and GCMS-QP2010 Ultra) equipped with a thermal conductive detector (TCD) and a flame ionization detector (FID). The degradation percentage of ethylene was represented in terms of  $C/C_0$ , where  $C$  is the concentration of remained ethylene at a certain time, and  $C_0$  is the initial concentration of ethylene injected.

## 3. Result and discussion

Fig. 1 shows the XRD patterns of as-prepared  $\text{Ga}_2\text{O}_3$  polymorphs. As shown in this figure, all the XRD peaks of as-prepared samples can be well identified to the characteristic reflections of  $\alpha$ - $\text{Ga}_2\text{O}_3$  (JCPDS no. 6-503),  $\beta$ - $\text{Ga}_2\text{O}_3$  (JCPDS no. 76-573),  $\gamma$ - $\text{Ga}_2\text{O}_3$  (JCPDS no. 20-426),  $\delta$ - $\text{Ga}_2\text{O}_3$  (JCPDS no. 06-529), respectively. The broad and poor diffraction peaks of both  $\gamma$ - $\text{Ga}_2\text{O}_3$  and  $\delta$ - $\text{Ga}_2\text{O}_3$  indicated the low crystallinity of the materials, which are also in accordance with literature.<sup>23–26</sup>

The morphologies of as-prepared  $\text{Ga}_2\text{O}_3$  polymorphs were shown in Fig. 2. As shown in Fig. 2(a) and (b), the as-prepared  $\alpha$ - and  $\beta$ - $\text{Ga}_2\text{O}_3$  exhibit similar morphologies, which are brick-like

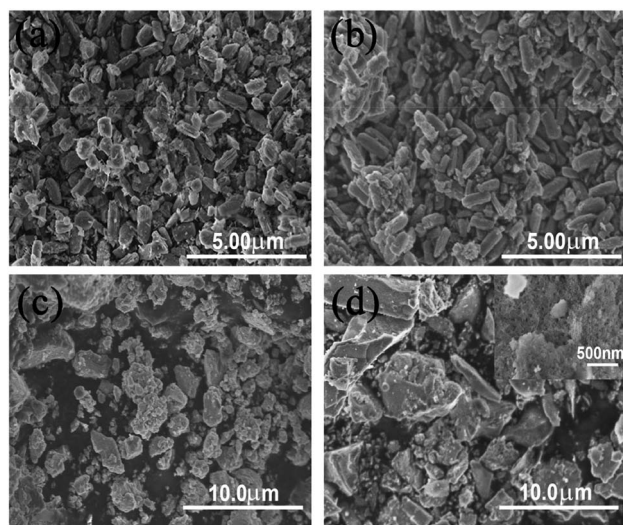


Fig. 2 The morphologies of as-prepared (a)  $\alpha$ - $\text{Ga}_2\text{O}_3$ , (b)  $\beta$ - $\text{Ga}_2\text{O}_3$ , (c)  $\gamma$ - $\text{Ga}_2\text{O}_3$ , and (d)  $\delta$ - $\text{Ga}_2\text{O}_3$ .

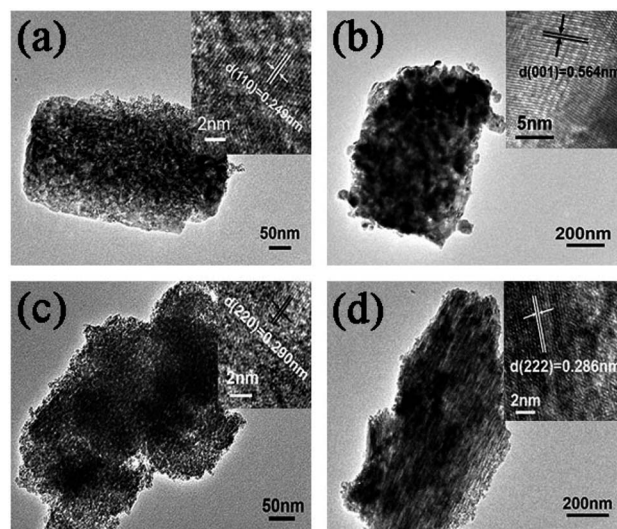


Fig. 3 TEM images of as-prepared (a)  $\alpha$ - $\text{Ga}_2\text{O}_3$ , (b)  $\beta$ - $\text{Ga}_2\text{O}_3$ , (c)  $\gamma$ - $\text{Ga}_2\text{O}_3$ , and (d)  $\delta$ - $\text{Ga}_2\text{O}_3$ .

particles consisted of stacked nanosheets with evenly distributed sizes. The length and width (thickness) of the brick-like particles are  $\sim 2$  and  $\sim 1$   $\mu\text{m}$ , respectively. Different from  $\alpha$ - and  $\beta$ - $\text{Ga}_2\text{O}_3$ , the as-prepared  $\gamma$ - and  $\delta$ - $\text{Ga}_2\text{O}_3$  exhibit irregular morphologies consisted of some small nanoparticles as shown in Fig. 2(c) and (d).

For a closer observation, HR-TEM characterizations of the as-prepared  $\text{Ga}_2\text{O}_3$  polymorphs were carried out as shown in Fig. 3. Although the morphologies of the four  $\text{Ga}_2\text{O}_3$  polymorphs are different as shown in Fig. 2, all these samples are consisted of some small nanoparticles according to the HR-TEM images as shown in Fig. 3. The clear lattice fringes as shown in the insets of Fig. 3 are corresponding to the (110) plane of  $\alpha$ - $\text{Ga}_2\text{O}_3$ , (001) plane of  $\beta$ - $\text{Ga}_2\text{O}_3$ , (220) plane of  $\gamma$ - $\text{Ga}_2\text{O}_3$ , (222) plane of  $\delta$ - $\text{Ga}_2\text{O}_3$ , which further confirmed the as-prepared samples are  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{Ga}_2\text{O}_3$ , respectively. The sizes of the nanoparticles building blocks are quite different, namely, the diameters of the nanoparticle building blocks are 6.6, 19.8, 4.1, and 6.3 nm for  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{Ga}_2\text{O}_3$ , respectively. And the BET surface areas of the as-prepared  $\text{Ga}_2\text{O}_3$  polymorphs were also measured as shown in Table 1. The surface areas for  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{Ga}_2\text{O}_3$  are 58.45, 17.75, 110.19, and 78.21  $\text{m}^2 \text{g}^{-1}$ , respectively. This is accordant with the HR-TEM observations, where smaller nanoparticles lead to higher surface areas.

Fig. 4 shows the diffused reflectance spectra of as-prepared  $\text{Ga}_2\text{O}_3$  polymorphs. As can be seen from this figure, the light

Table 1 Summary of the physicochemical properties of the  $\text{Ga}_2\text{O}_3$  polymorphs

	$\alpha$ - $\text{Ga}_2\text{O}_3$	$\beta$ - $\text{Ga}_2\text{O}_3$	$\gamma$ - $\text{Ga}_2\text{O}_3$	$\delta$ - $\text{Ga}_2\text{O}_3$
BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	58.45	17.75	110.19	78.21
Band gap (eV)	4.86	4.36	4.43	4.33
Reaction rate constant ( $\text{h}^{-1}$ )	0.661	0.148	0.861	0.217





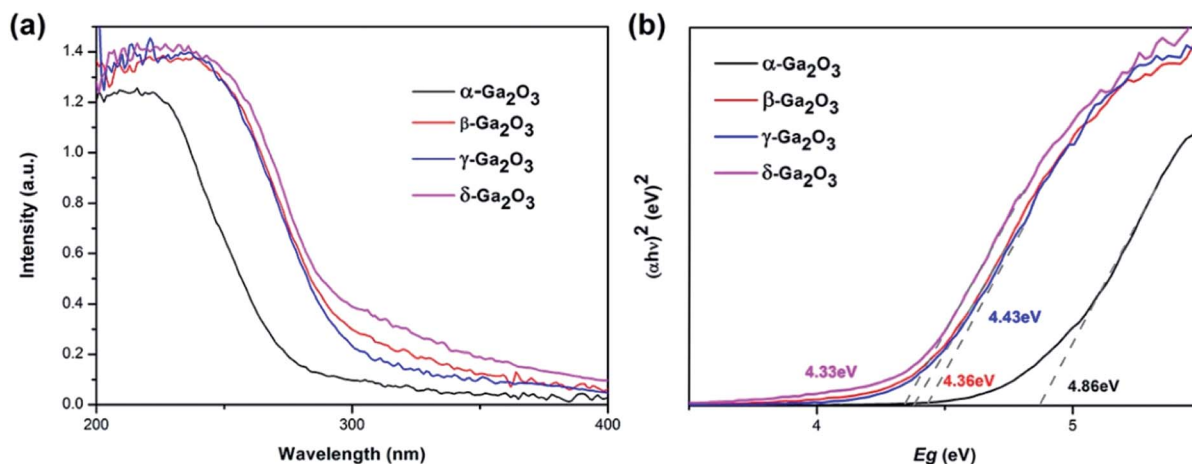


Fig. 4 (a) The diffused reflectance spectra and (b) Tauc's plots of as-prepared  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>.

absorption edge of  $\beta$ -,  $\gamma$ -, and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> is almost identical, which lies at  $\sim 300$  nm. But the absorption edge of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is much shorter, lying at  $\sim 270$  nm. And as shown in the Tauc's plots of Ga<sub>2</sub>O<sub>3</sub> polymorphs in Fig. 4(b), the band gap for  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> is calculated to be 4.86, 4.36, 4.33, 4.43 eV, respectively.

The photocatalytic activity of as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs was evaluated by the degradation of ethylene under UV

irradiation. For comparison, P25 was also employed to decompose ethylene under identical condition. As shown in Fig. 5(a), before illumination, dark adsorption experiments were carried out in dark for 2 hours. After the adsorption equilibrium, only a small amount of ethylene was adsorbed by the as-prepared samples. And the ethylene concentrations decrease from 1100 ppm to 1057, 1072, 1096, 1091, 1060 ppm for  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -

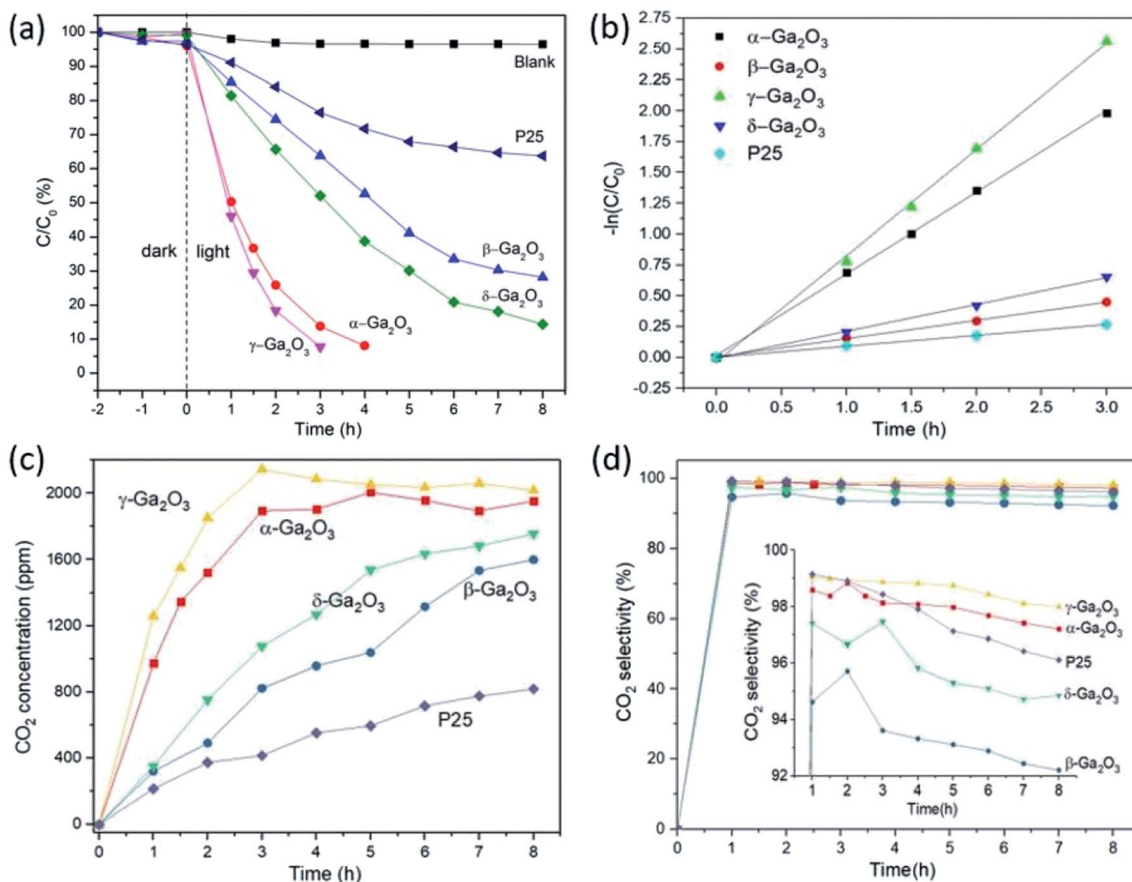


Fig. 5 (a) The photocatalytic ethylene degradation plots and (b) the degradation rate constants over as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs and P25. (c) The amount of CO<sub>2</sub> produced during the photocatalytic experiments and (d) the percentage of CO<sub>2</sub> in the final products over the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs.



Ga<sub>2</sub>O<sub>3</sub> and P25, respectively. As shown in the photocatalytic ethylene degradation plots in Fig. 5(a),  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> exhibits the highest photocatalytic activity among these Ga<sub>2</sub>O<sub>3</sub> polymorphs, which can decompose the ethylene gas in 3 h. And the photocatalytic activity of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is slightly lower than that of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, where the ethylene can be decomposed in 4 h.  $\beta$ - and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> are less photocatalytic reactive comparing to  $\gamma$ - and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, which can decompose 72% and 86% after irradiated under UV light for 8 h, respectively. However, all the Ga<sub>2</sub>O<sub>3</sub> polymorphs exhibit higher activity than P25, where only ~36% of ethylene can be decomposed over P25 under identical conditions in 8 h. The photocatalytic degradation rates of the Ga<sub>2</sub>O<sub>3</sub> polymorphs and P25 were also calculated as shown in Fig. 5(b), which exhibit a pseudo-first-order relationship. The degradation rate constant for  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> and P25 is 0.661, 0.148, 0.861, 0.217 and 0.089 h<sup>-1</sup>, respectively (Table 1). Apparently, the highest ethylene degradation rate of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> is nearly 10 times as high as that of P25. As the activity of the photocatalysts is closely related to their specific surface areas, the highest photocatalytic activity of as-prepared  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> could be mainly ascribed to the largest surface areas among these Ga<sub>2</sub>O<sub>3</sub> polymorphs. By normalizing the degradation rate constants to the specific surface areas,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> exhibited the highest photocatalytic activity with the normalized rate constant of 0.01132 m<sup>2</sup> (g h)<sup>-1</sup>. While, the normalized constant for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>,  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, P25 is 0.00836, 0.00781, 0.00278 and 0.00197 m<sup>2</sup> (g h)<sup>-1</sup>, respectively. Thus, the photocatalytic activity of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs after normalizing to the surface areas should follow the order:  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> >  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>.

As shown in Fig. 5(c), the concentration of CO<sub>2</sub> increases constantly with the degradation of ethylene. As the CO<sub>2</sub> is mainly produced by the photocatalytic degradation of ethylene, the amount of CO<sub>2</sub> produced over different photocatalysts are mainly determined by the photocatalytic degradation of ethylene and accordant with the degradation rate constants as shown in Fig. 5(a) and Table 1. By analyzing the products during

the photocatalytic experiments, CO<sub>2</sub> was found to be the main products as shown in Fig. 5(d), which take part in more than 90% of the final products for all the samples. However, the percentage of CO<sub>2</sub> produced over different Ga<sub>2</sub>O<sub>3</sub> polymorphs varies a lot as shown in the inset of Fig. 5(d). In detail, the percentage of CO<sub>2</sub> is the highest in  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, which takes 98% of the final products at the end of the photocatalytic experiments. And the percentage of CO<sub>2</sub> for  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, P25,  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is 97.2, 96.1, 94.8, and 92.2%, respectively. More interestingly, the percentage of CO<sub>2</sub> in the products gradually decreased with the increase of the photocatalytic experiment time. This indicates part of the produced CO<sub>2</sub> could be further converted to other secondary products, such as CO and CH<sub>4</sub>, which would be unfavorable for the practical applications during the postharvest storage of fruits and vegetables. From this aspect,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> with highest photocatalytic ethylene degradation rate and highest CO<sub>2</sub> conversion efficiency could be the most suitable candidate among the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs for photocatalytic ethylene degradation.

To evaluate the cycling stability of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, four consecutive-cycle ethylene degradation experiments were conducted. As shown in Fig. 6, the sample does not show any particular loss of photocatalytic activity for ethylene degradation during the repeated experiments. Therefore,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> can work as an effective photocatalyst for ethylene degradation with good stability.

To probe the mechanism for the different photocatalytic performances of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs, the band structures were investigated by XPS valence spectra. As shown in Fig. 7(a), the valence band maximum (VBM) of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs were determined by extrapolating a linear fit of the low binding energy edge of the valence band spectra to line fitted to the instrument background. The VBM of as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs can be determined according to the formula:

$$E_{\text{VB}} = E + \phi_{\text{Al}} - 4.5$$

where  $E_{\text{VB}}$  is the position of VBM vs. reversible hydrogen electrode (RHE),  $E$  is the position of VBM obtained from XPS valence spectra vs. the aluminum holder,  $\phi_{\text{Al}}$  is the work function of aluminum (4.2 eV vs. vacuum level).<sup>27</sup> The calculated VBM for  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> lies at 3.54, 2.87, 3.04, and 2.75 eV (vs. RHE), respectively. Combining the band gaps estimated from the diffused reflectance spectra as shown in Fig. 4(b), the band diagrams for the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs can be obtained as shown in Fig. 7(b). According to the calculated band structures of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs, the oxidability of the photogenerated holes for the Ga<sub>2</sub>O<sub>3</sub> polymorphs should follow the order:  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>, and the reducibility of the photogenerated electrons follow the order:  $\delta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>.

As the photocatalytic ethylene degradation into CO<sub>2</sub> is an oxidation process, the photocatalytic ethylene degradation activity of as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs is mainly determined by their VBM, and should follow the order:  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> >  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> >  $\delta$ -Ga<sub>2</sub>O<sub>3</sub>. This order is almost accordant with the

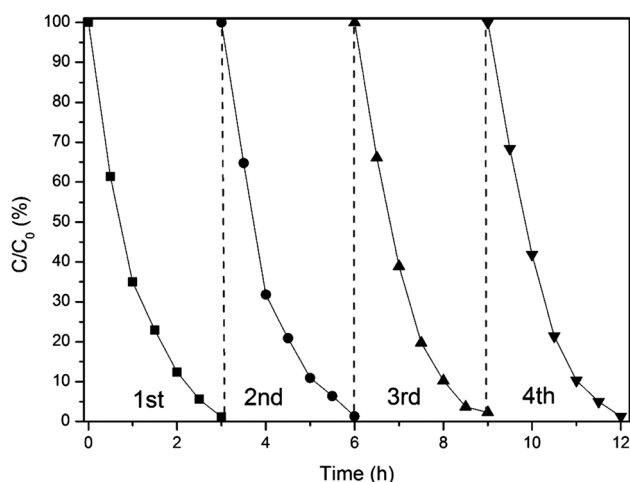


Fig. 6 Four consecutive-cycles of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> for photocatalytic ethylene degradation.



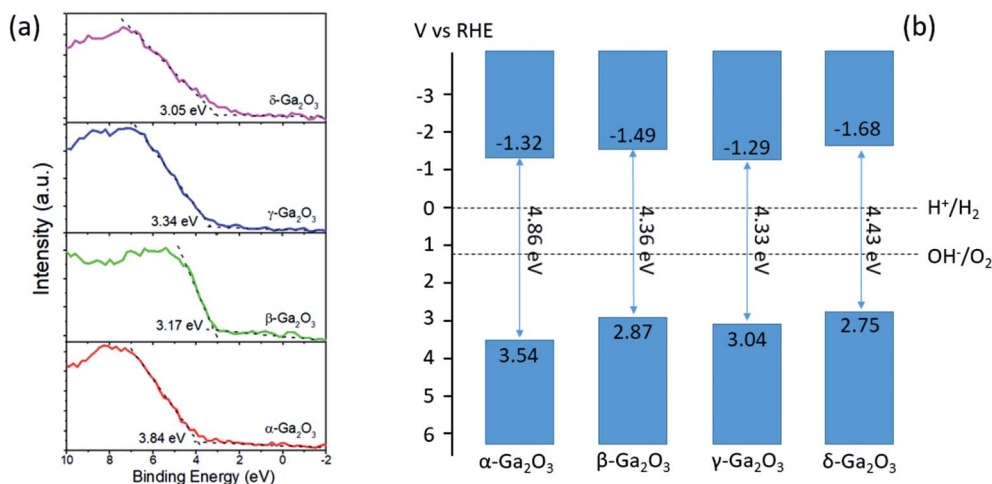


Fig. 7 (a) The XPS valence spectra of as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs. (b) The calculated band diagrams for α-, β-, γ-, and δ-Ga<sub>2</sub>O<sub>3</sub>, respectively.

normalized degradation rate constants for the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs except for β-Ga<sub>2</sub>O<sub>3</sub>, where β-Ga<sub>2</sub>O<sub>3</sub> with more negative VBM is more reactive than γ-Ga<sub>2</sub>O<sub>3</sub>. This could be due to the higher crystallinity of β-Ga<sub>2</sub>O<sub>3</sub> as evidenced by the sharper XRD diffraction peaks as shown in Fig. 1 than γ-Ga<sub>2</sub>O<sub>3</sub>, because photogenerated charge carriers recombine more quickly in poorly crystallized photocatalysts. Besides the effects of VBM and crystallinity, the photocatalytic performances of photocatalysts were also closely related to the surface areas of the photocatalysts. Thus, although the normalized degradation rate constant of α- and β-Ga<sub>2</sub>O<sub>3</sub> is higher than γ-Ga<sub>2</sub>O<sub>3</sub>, the overall photocatalytic performance of γ-Ga<sub>2</sub>O<sub>3</sub> is the highest among the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs owing to the highest specific surface areas. Additionally, with the most positive CBM, γ-Ga<sub>2</sub>O<sub>3</sub> produces the least CO during the photocatalytic ethylene degradation among the Ga<sub>2</sub>O<sub>3</sub> polymorphs. Both of these attributes are favorable for photocatalytic ethylene degradation during the post-harvest storage of fruits and vegetables, which make γ-Ga<sub>2</sub>O<sub>3</sub> a potential candidate for practical photocatalytic ethylene degradations.

## 4. Conclusions

In this work, we fabricated four Ga<sub>2</sub>O<sub>3</sub> polymorphs and investigated their photocatalytic activities on ethylene degradation. According to the experimental results, all the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs exhibit higher photocatalytic activities on ethylene degradation than P25 under UV light irradiation. The normalized photocatalytic ethylene degradation rate constant of the as-prepared Ga<sub>2</sub>O<sub>3</sub> polymorphs follows the order: α-Ga<sub>2</sub>O<sub>3</sub> > β-Ga<sub>2</sub>O<sub>3</sub> > γ-Ga<sub>2</sub>O<sub>3</sub> > δ-Ga<sub>2</sub>O<sub>3</sub>, which could be ascribed to the synergistic effects of the VBM position and the crystallinity of the samples. Due to the highest surface area, γ-Ga<sub>2</sub>O<sub>3</sub> exhibits the highest photocatalytic activity for ethylene degradation among these Ga<sub>2</sub>O<sub>3</sub> polymorphs, which has a degradation rate constant 10 times as high as that of P25. Furthermore, γ-Ga<sub>2</sub>O<sub>3</sub> produces the least CO during ethylene degradation due to its more positive CBM. Based on these attributes, γ-Ga<sub>2</sub>O<sub>3</sub> is

regarded as a potential candidate for photocatalytic ethylene degradations that could be applied in the post-harvest storage of fruits and vegetables.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (21333006, 21573135, and 51602179), the National Basic Research Program of China (the 973 program, 2013CB632401). B. B. H. acknowledges the support from Taishan Scholars Program of Shandong Province, and Z. Y. W. acknowledges support from Young Scholars Program of Shandong University (2015WLJH35).

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