# From Gallium-Based Supramolecular Square Nanoplates to $\gamma\text{-}Ga_2O_3$ Layer Nanosheets \*

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# **Experimental Section**

*Preparation of the nanostructured Supramolecular materials (NSMs):* In the preparation experiments, all the reagents <sup>5</sup> were analytical grade and were used without further purification. The NSMs were synthesized by a grinding process. For example, gallium acetylacetonate (GAA) (200 mg, 0.544 mmol) and β-cyclodextrin (β-CD) (617 mg, 0.544 mmol) was added to an agate mortar, and the mixture was ground for 30 min at room temperature and dried in a vacuum desiccator over phosphoric oxide. The sample obtained at the temperature was named as β-CD-GAA-1, and the other sample obtained at 353 K was named as β-CD-GAA-2. The other NSMs were obtained at different temperatures: 273, 283, 313 and 333 K. <sup>10</sup> <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) data of β-CD, GAA and GAA-β-CD-1 are as follows. <sup>1</sup>H NMR (400 MHz, 298 K) of β-CD: δ 5.085 (d, 7H, J = 3.7 Hz, C<sub>1</sub>H of β-CD), 3.965 (t, 7H, J = 9.5, C<sub>3</sub>H of β-CD), 3.893 (s, 7H, C<sub>6</sub>H of β-CD), 3.855 (s, 7H, C<sub>5</sub>H of β-CD), 3.680 (d, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.594 (d, 7H, J = 9.0, C<sub>4</sub>H of β-CD). <sup>1</sup>H NMR (400 MHz, 298 K) of β-CD-GAA-1: δ 5.076 (d, 7H, J = 3.5 Hz, C<sub>1</sub>H of β-CD), 3.947 (t, 7H, J = 9.5, C<sub>3</sub>H of β-CD), 3.874 (d, 7H, J = 4.3, <sup>15</sup> C<sub>6</sub>H of β-CD), 3.830 (s, 7H, C<sub>5</sub>H of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, CH of β-CD), 3.616 (t, 7H, J = 3.7, C<sub>2</sub>H of β-CD), 3.587 (d, 7H, J = 9.2, C<sub>4</sub>H of β-CD), 5.165 (c, H J = 3.5 Hz, C

(s, H, J = 3.5 Hz, CH of GAA), 2.020 (d, 3H, J = 6.5 Hz, CH<sub>3</sub> of GAA).

**Preparation of the**  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> **materials:** The three  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> materials were synthesized by a sintering process of the  $\beta$ -CD-GAA-2 at different temperatures. For example, the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 was prepared by sintering of the  $\beta$ -CD-GAA-2 at 673 K for <sup>20</sup> 3.5 h. The other two  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples were obtained by sintering of the  $\beta$ -CD-GAA-2 at 623 and 723 K for 3.5 h. The  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-2 was synthesized by sintering of the free GAA (200 mg, 0.544 mmol) at 673K for 3.5 h.

*Material characterization:* XRD measurements were recorded on a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu K $\alpha$  radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range of  $^{25} 20^\circ \le 2\theta \le 80^\circ$ . Field emission scanning electron microscope (FE-SEM) images were performed by using a Supra 40 operated at 5 kV. Thermogravimetry (TG) was performed on a DTGA-60H thermogravimetric analyzer at a constant heating rate of 10.0 K min<sup>-1</sup> under a nitrogen atmosphere with a gas flow of 25 mL min<sup>-1</sup>. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Equinox 55 spectrometer with KBr pellets in the range of 400~4000 cm<sup>-1</sup> with a resolution of less than 0.09 cm<sup>-1</sup>. The <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 30 300 NMR solid spectrometer at 400 MHz at ambient temperature unless otherwise stated. Nitrogen adsorption/desorption isotherms were obtained using Micromeritics ASAP-2000 at 77 K. UV-Vis diffuse-reflectance spectrum (DRS) was

recorded employing a Shimadzu DUV-3700 spectrophotometer in the wavelength between 220 and 2000 nm. Barium sulfate powder was used as the reflectance standard material to adjust baseline parameters. Photoluminescence (PL) measurements were performed on a Perkin Elmer Luminescence spectrometer L550B at room temperature (excited at 325 nm).

**Photoresponse properties:** The solid-state device was made of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and the ends of  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> were connected with two Ti/Au electrodes. The fabrication process is as follows. First, a Ti/Au film with a thickness of about 200 nm was deposited by magnetron sputtering (Sputter-Lesker Lab18) on a glass substrate. Then, a channel with a width of about 40 µm was <sup>40</sup> created through a laser etching process. At the same time,  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> was ground in a mortar and suspended in ethanol using

an ultrasonic bath for half an hour. After that, 1  $\mu$ L of the suspension was dropped in the channel between the two Ti/Au electrodes. At last, the device was dried in an oven at 353 K for 2 h. A 254 nm light (XS-T5, 6W) was illuminated on  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>, and the photoresponse performance was measured by a CHI 760 electrochemical workstation with a two-electrode configuration. The power density is 28.4  $\mu$ W·cm<sup>-2</sup>.



**Figure S1.** The fractional mass loss per second ( $\nu$ , % s<sup>-1</sup>) as a function of temperature for GAA,  $\beta$ -CD,  $\beta$ -CD-GAA-1, at heating rate of 10 K min<sup>-1</sup>. The maximum decomposition temperature of the GAA and  $\beta$ -CD in the supermolecule were advanced by about 21 and 16 K, respectively.



**Figure S2.** A) The UV-Vis spectra and B) Job's plot of the solutions (total moles of solutes, TM) of GAA and  $\beta$ -CD (the R is a molar ratio of GAA to the TM).



Figure S3. The FE-SEM images of the  $\beta$ -CD-GAA samples obtained at 273 (A) and 283 K (B).



**Figure S4.** The XRD patterns of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples obtained by sintering of the  $\beta$ -CD-GAA-2 at 623 and 723 K for 2 h in air.



**Figure S5.** The XRD patterns of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples and the JCPDS cards of  $\gamma$ -,  $\alpha$ -,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, and MgAl<sub>2</sub>O<sub>4</sub>.



**Figure S6.** The FE-SEM images of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples obtained by sintering of the  $\beta$ -CD-GAA-2 at 623 (A) and 723 K (B) for 2 h in air.



**Figure S7.** The N<sub>2</sub> adsorption-desorption isotherms and pore size distributions (inset) of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 (A) and -2 (B).

<sup>5</sup> The permanent porosity of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 and -2 samples was confirmed by gas sorption isotherm measurements performed in liquid nitrogen. The nitrogen adsorption–desorption isotherm (Figure S7) indicates a *type IV* isotherm profile with a *type H3* loop, which is often observed with aggregates of plate-like particles giving rise to slit-shaped pores.<sup>[1,2]</sup> Thus, the slit-shaped pores between the aggregated particles might be the origin of the porosity in the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> samples.

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Figure S8. The room temperature UV-Vis DRS of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 and -2.

Figure S9. The calculation of the exciton Bohr radius of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>.

The exciton Bohr radius ( $a_B$ ) of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> can be calculated using the equation, <sup>3-4</sup>

$$a_{\rm B} = \frac{h^2 \varepsilon \varepsilon_0}{\pi e^2 \mu}$$

s where  $\varepsilon$ ,  $\varepsilon_0$ , *h* and *e* are the static dielectric constant, permittivity of free space, Planck constant and electron charge, respectively.  $\mu$  is the reduced mass of an electron-hole pair, and it can be determined by the equation:

$$1/\mu = 1/m_{\rm e} + 1/m_{\rm h}$$

where  $m_e$  and  $m_h$  are the effective mass of an electron and hole, respectively.<sup>4</sup> The  $m_e$  is small and <sup>10</sup> almost isotropic, having a value of 0.27~0.28  $m_0$ , where  $m_0$  is the electron mass. The  $m_h$  values along

the  $\Gamma$ -Z direction and  $\Gamma$ -A direction were estimated to be around 40  $m_0$  and 0.40  $m_0$ , respectively.<sup>5</sup> The  $\varepsilon$  value is about 10.0,<sup>6</sup> and the calculated  $a_B$  of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub> is less than 3.29 nm. Thus, the shift of 0.22 eV in the bandgap from the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-2 (4.98 eV) to  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 (4.76 eV) should not arise from the quantum confinement effect since the diameter of the nanoparticles is no less than 3.29 nm. Therefore,

<sup>15</sup> we consider that the difference in the band gap of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-**2** and  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-**1** is due to the structural difference between them, since the structural difference often causes different electronic band structures in metal oxides.

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**Figure S10.** The PL spectra of the  $\gamma$ -Ga<sub>2</sub>O<sub>3</sub>-1 (black line) and -2 (red line). The blue arrow indicates the red shift of the maximum emission positions.

Namamataniala	LC	DC	RT	DT	LDR	Wavelength	PD	Bias	Ref.
Nanomateriais	/nA	/nA	/s	/s		/nm	$/\mu W \cdot cm^{-2}$	/ <b>V</b>	
γ-Ga <sub>2</sub> O <sub>3</sub> -1	$1.48 \times 10^{4}$	0.9	0.06	0.06	$1.64 \times 10^4$	254	28.4	0.1	This work
γ-Ga <sub>2</sub> O <sub>3</sub> - <b>2</b>	$2.01 \times 10^{3}$	2.61	0.2	0.2	770	254	28.4	0.1	This work
$\gamma$ -Ga <sub>2</sub> O <sub>3</sub> nanospheres	$1.83 \times 10^{3}$	18	0.1	0.1	$2.29 \times 10^{3}$	254	28.4	0.1	7
$\gamma$ -Ga <sub>2</sub> O <sub>3</sub> nanoflowers	66	0.3	< 0.1	-	220	254	-	0.5	8
$\gamma$ -Ga <sub>2</sub> O <sub>3</sub> microspheres	54	4.4	-	-	12	254	-	0.5	8
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> nanospheres	60	1.4	_	-	43	254	-	0.5	8
β-Ga <sub>2</sub> O <sub>3</sub> fiim	$8 \times 10^{2}$	40	-	0.07	20	254	45	10	9
β-Ga <sub>2</sub> O <sub>3</sub> nanowires	0.56	0.026	0.5	-	21	254	-	20	10
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> thin film	4	0.31	0.62	0.83	13	254	60	1	11
β-Ga <sub>2</sub> O <sub>3</sub> film	$2.9 \times 10^{3}$	0.62	_	-	4.7	255	17	20	12
β-Ga <sub>2</sub> O <sub>3</sub> nanowires	6	$2 \times 10^{-4}$	-	< 0.02	$3 \times 10^{4}$	254	$2 \times 10^{3}$	50	13
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> nanowires	10	0.015	0.22	0.09	666	254	-	8	14
β-Ga <sub>2</sub> O <sub>3</sub> microwires	$1.1 \times 10^{2}$	2.1	1×10-4	9×10 <sup>-4</sup>	52	251	-	2	15
β-Ga <sub>2</sub> O <sub>3</sub> flakes	$1.80 \times 10^{3}$	23	_	-	78	254	-	10	16
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> nanobelts	-	-	91	36	100	250	0.72	30	17
$\beta$ -Ga <sub>2</sub> O <sub>3</sub> nanobelts	< 0.1	$< 10^{-4}$	< 0.3	< 0.3	10 <sup>3</sup>	250	98.3	5	18
β-Ga <sub>2</sub> O <sub>3</sub> nanosheets	2.5	0.2	0.03	0.06	12	254	500	10	19

Table S1. Photoresponses of different Ga<sub>2</sub>O<sub>3</sub> materials for solar-blind photodetection.

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