## **Electronic Supplementary Information (ESI) :**

Self-Assembly of single-crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates to columnar superstructures: controllable synthesis, growth mechanism, and properties

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Sample		Reaction		Sizes		
number	$C(\mathrm{Fe}^{3+})$	time	Morphology	diameter	thickness	length
α-Fe <sub>2</sub> O <sub>3</sub> -1	0.01 M	30 h	column-like (Fig. 3a)	~120 nm	~20 nm	~220 nm
α-Fe <sub>2</sub> O <sub>3</sub> -2	0.02 M	30 h	column-like (Fig. 2a)	~380 nm	~40 nm	$\sim 2 \ \mu m$
α-Fe <sub>2</sub> O <sub>3</sub> -3	0.03 M	30 h	column-like (Fig. 3b)	~750 nm	~80 nm	$\sim 2.2 \ \mu m$
α-Fe <sub>2</sub> O <sub>3</sub> -4	0.02 M	5 h	plates (Fig. S6b)	~240 nm	~30 nm	-
α-Fe <sub>2</sub> O <sub>3</sub> -5	0.04 M	30 h	plates (Fig. 3c)	~1.5 µm	~240 nm	-
α-Fe <sub>2</sub> O <sub>3</sub> -6	0.1 M	30 h	plates (Fig. 3d)	~2.5 µm	~500 nm	-

**Table S1.** The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals obtained by a hydrothermal route in the presence of glycerin (1 mL) at 140 °C with different concentration of Fe<sup>3+</sup> and reaction time.

		Additives		Reaction	Yeilds		
Sample number	C <sub>Fe3+</sub>	polyols	Surfactant	conditions	(wt %)	Morphology	
α-Fe <sub>2</sub> O <sub>3</sub> -7	0.02 M	1 mL EG <sup>[a]</sup>	absence	140 °C for 30 h	~80	sphere (Fig. S5a)	
α-Fe <sub>2</sub> O <sub>3</sub> -8	0.02 M	1 mL DPE <sup>[a]</sup>	absence	140 °C for 30 h	~85	sphere (Fig. S5b)	
α-Fe <sub>2</sub> O <sub>3</sub> -9	0.02 M	1 mL NPA <sup>[a]</sup>	absence	140 °C for 30 h	~85	aggregated sphere (Fig. S5c)	
α-Fe <sub>2</sub> O <sub>3</sub> -10	0.02 M	1 mL PEG-200 <sup>[a]</sup>	absence	140 °C for 30 h	~80	aggregated sphere (Fig. S5d)	
α-Fe <sub>2</sub> O <sub>3</sub> -11	0.02 M	without polyols	absence	140 °C for 30 h	~60	polyhedron (Fig. S5e)	
α-Fe <sub>2</sub> O <sub>3</sub> -12	0.02 M	2 mL glycerin	absence	140 °C for 30 h	~90	plates (Fig. S5f)	
α-Fe <sub>2</sub> O <sub>3</sub> -13	0.02 M	5 mL glycerin	absence	140 °C for 30 h	~50	plates (Fig. S5g)	
α-Fe <sub>2</sub> O <sub>3</sub> -14	0.02 M	1 mL glycerin	absence	120 °C for 30 h	~45	plates (Fig. S4a)	
α-Fe <sub>2</sub> O <sub>3</sub> -15	0.02 M	1 mL glycerin	absence	130 °C for 30 h	~75	column-like (Fig. S4b)	
α-Fe <sub>2</sub> O <sub>3</sub> -16	0.02 M	1 mL glycerin	absence	150 °C for 30 h	~98	column-like (Fig. S4c)	
α-Fe <sub>2</sub> O <sub>3</sub> -17	0.02 M	1 mL glycerin	absence	160 °C for 30 h	~98	column-like (Fig. S4d)	
α-Fe <sub>2</sub> O <sub>3</sub> -18	0.02 M	1 mL glycerin	CTAB <sup>[a]</sup>	140 °C for 30 h	~80	column-like (Fig. 4a)	
α-Fe <sub>2</sub> O <sub>3</sub> -19	0.02 M	1 mL glycerin	CTAC <sup>[a]</sup>	140 °C for 30 h	~85	column-like (Fig. 4b)	
α-Fe <sub>2</sub> O <sub>3</sub> -20	0.02 M	1 mL glycerin	PVP <sup>[a]</sup>	140 °C for 30 h	~60	platelet (Fig. 4c)	
α-Fe <sub>2</sub> O <sub>3</sub> -21	0.02 M	1 mL glycerin	PVA <sup>[a]</sup>	140 °C for 30 h	~60	plates (Fig. 4d)	
α-Fe <sub>2</sub> O <sub>3</sub> -22	0.02 M	1 mL glycerin	SDS <sup>[a]</sup>	140 °C for 30 h	~55	particle (Fig. 4e)	
α-Fe <sub>2</sub> O <sub>3</sub> -23	0.02 M	1 mL glycerin	SDBS <sup>[a]</sup>	140 °C for 30 h	~50	particle (Fig. 4f)	
α-Fe <sub>2</sub> O <sub>3</sub> -24	0.02 M	1 mL glycerin	absence	140 °C for 2 h	~35	particle (Fig. S6a)	
α-Fe <sub>2</sub> O <sub>3</sub> -25	0.02 M	1 mL glycerin	absence	140 °C for 10 h	~80	platelet (few) and column-	
2 9						like (Fig. S6c)	
α-Fe <sub>2</sub> O <sub>3</sub> -26	0.02 M	1 mL glycerin	absence	140 °C for 20 h	~ 90	plates (very few) and	
a 10203 20		0.9				column-like (Fig. S6d)	

**Table S2.** The yields and morphologies of products obtained with different experimental parameters such as temperature, types of polyol and surfactant, and reaction time.

[a] EG = ethylene glycol, DPE = diethylene glycol, NPA = n-propyl alcohol, PEG-200= poly(ethylene glycol 200), CTAB=cetyltrimethylammonium chloride bromide, CTAC=cetyltrimethylammonium chloride, PVP= polyvinylpyrrolidone, PVA=poly(vinyl alcohol), SDS= sodium dodecyl sulfonate, SDBS=sodium dodecyl benzene sulfonate.



Fig. S1 (a) Photograph of the gas sensor, and (b) working principle of the gas sensing measurement system ( $V_h$ : heating voltage;  $V_{out}$ : signal voltage and  $R_L$ : load resistor).



Fig. S2 High resolution SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-2, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-3, (c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-5, and (d)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-6.



Fig. S3 XRD patterns of the obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals with different sizes: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-5, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-6, and (c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-1, respectively.



Fig. S4 SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals formed at different temperatures of (a) 120 °C, (b) 130 °C, (c) 150 °C, and (d) 160 °C with the same reaction time of 30 h.



**Fig. S5** SEM images of the samples obtained at different polyols of (a) EG, (b) DPE, (c) NPA, (d) PEG-200, (e) without polyol, (f) with glycerin/H<sub>2</sub>O=2:38 (v/v), and (g) with glycerin/H<sub>2</sub>O=5:35 (v/v), respectively, when keeping other conditions constant.



Fig. S6 SEM images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals obtained at 140 °C with different reaction times of (a) 2, (b) 5, (c) 10, and (d) 20 h, respectively.



Fig. S7 FT-IR spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-5, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-6, (c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-1, (d)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-3, (e)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-4, and (f)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-2.



**Fig. S8** Responses of the (a) plate-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-4) and (b) CODS  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-2) sensors upon exposure to nine kinds of organic vapors (100 ppm) at a working temperature of 280 °C, respectively.