Electronic Supplementary Information (ESI):

Facile synthesis of single-crystalline hollow $\alpha$-Fe$_2$O$_3$ nanospheres with
gas sensing properties

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1. Experimental

1.1 Materials

Zinc acetate dihydrate, thiourea, cyclohexylamine (CHA), ethanol and the reference gas sensing reagents were purchased from Beijing Chemical Factory. FeCl$_3$.6H$_2$O was purchased from Tianjin Huadong Chemical Industry. All of the reagents were of analytic grade and used as received without further purification. Deionized water was used throughout.

1.2 General characterization

X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å) was assessed to determine crystalline structure of the samples Rigaku D/Max 2550. The morphology of the samples is obtained by scanning electron microscope (SEM) of JEOL JSM 6700F. Transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) were determined by FEI Tecnai G2S-Twin. XPS spectra were recorded on an ESCALAB 250 X-ray photoelectron spectrometer, using a monochromated X-ray source (Al Kα h = 1486.6 eV). Raman spectra were characterized with Horiba Jobin Yvon LabRAM ARAMIS with 633 nm He-Ne laser excitation. Nitrogen absorption and desorption isotherms was performed on Micromeritics ASAP 2020M system.

1.3 Preparation of ZnS-CHA Nanohybrid

The ZnS-CHA nanohybrid material was prepared by following the previously-reported solvothermal procedures with slight variations.\(^1\) Zinc acetate dihydrate (0.32 g, 1.5 mmol) as the zinc source and thiourea (0.255 g, 3 mmol) as the sulfur source were added to CHA (40 mL) and stirred vigorously. The mixture was sealed and heated at 120 °C for 20 h in a 50 mL PTFE-lined stainless steel autoclave. The white ZnS-CHA precipitate was obtained after cooling down to room temperature, which was washed several times with ethanol and dried at 60 °C for 6 h.

1.4 Synthesis of single-crystalline hollow α-Fe$_2$O$_3$ nanospheres

FeCl$_3$.6H$_2$O (0.16 g) with the as prepared ZnS-CHA nanocomposite (0.03 g) were stirred in 20 mL deionized water for 20 min, and then the mixture was sealed in a 30 mL PTFE-lined stainless steel autoclave and heated at 160 °C for 24 h. After cooling down to room temperature, the red α-Fe$_2$O$_3$ precipitate was harvested and washed several times with ethanol and dried at 60 °C 6 h for further use.
Fig. S1 (A) XRD pattern; (B) IR spectrum; (C) TG analysis; high resolution XPS spectra of (D) Zn 2p, (E) S 2p and (F) N 1s for the ZnS-CHA nanocomposite.

Fig. S2 SEM image of the ZnS-CHA nanohybrid.
**Fig. S3** SEM images of the products obtained at (A) 30 min, (B) 1 h, (C) 6 h, (D) 8 h, (E) 24 h, and (F) low magnification TEM for 24 h.

**Scheme S1.** Scheme for synthesis of the hollow single-crystalline $\alpha$-Fe$_2$O$_3$ nanospheres.
Fig. S4 High resolution XPS spectra (A) Fe 2p and (B) O 1s of the single-crystalline hollow Fe$_2$O$_3$.

Fig. S5 Contrast SEM images of the obtained Fe$_2$O$_3$ with different reaction conditions named (A) Fe$_2$O$_3$-1; (B) Fe$_2$O$_3$-2; (C) Fe$_2$O$_3$-3; (D) Fe$_2$O$_3$-4, respectively.
Fig. S6 SEM images of the different size Fe$_2$O$_3$ nanospheres with multiplied Fe$^{3+}$ source (A) 0.16 g; (B) 0.32 g; (C) 0.48 g and (D) 0.64 g FeCl$_3$6H$_2$O.

Fig. S7 (A) TEM and (B) HRTEM images of the Fe$_2$O$_3$ obtained at 6 h; (C) TEM and (D) HRTEM images of the Fe$_2$O$_3$-1 (In control experiment section (1)).
**Fig. S8** Nitrogen adsorption-desorption isotherm of (A) the single-crystalline hollow Fe$_2$O$_3$ nanospheres and (B) Fe$_2$O$_3$-1.

**Fig. S9** Magnification curve of the single-crystalline hollow Fe$_2$O$_3$ nanospheres towards 500 ppm ethanol.
Fig. S10 Stability sensing measurement to ethanol of the single-crystalline hollow Fe$_2$O$_3$ nanospheres.

Reference