Supplementary information

Template-free construction of hollow $\alpha$-Fe$_2$O$_3$ hexagonal nanocolumns with exposed special surface for advanced gas sensing properties

Linqiang Sun,$^a$ Xiao Han,$^a$ Kai Liu,$^a$ Shan Yin,$^a$ Qiaoli Chen,$^b$ Qin Kuang,$^b$ Xiguang Han$^*$,$^a$, Zhaoxiong Xie$^b$, Chao Wang$^a$

$^a$Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Department of Chemistry, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou, 221116 (P. R. China)
E-mail: xghan@jsnu.edu.cn

$^b$State Key Laboratory of Physical Chemistry of Solid Surfaces & Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Experimental Section:

Reagents: Iron(III) chloride hexahydrate (FeCl$_3$•7H$_2$O), Sodium hydroxide (NaOH), Sodium dodecylbenzenesulfonate (SDBS) were purchased from commercial suppliers (Sinopharm Chemical Regent) and used as received without further purification.

Synthesis and characterization of Hollow $\alpha$-Fe$_2$O$_3$ hexagonal nanocolumns (HHCPs):

In a typical synthesis of the product (HHCPs), FeCl$_3$•6H$_2$O (0.1 g, 0.37 mmol) was added into the mixed solvent of ethanol and distilled water (15 mL, v/v of 1:1) under intense stirred treatment for 10 minutes, and then NaOH solution (40 $\mu$L, 2 M) and SDBS (0.15 g, 0.43 mmol) was added into the solution, and keep to stir for 10 minutes. The resulting solution was transferred into 25 ml a Teflon-lined stainless-steel autoclave and was kept at 200 °C for 6 h. The products (SEPs) and (HEPs) can be respectively obtained after 1 h and 2 h. The red products were collected by centrifuge and washed by deionized water and ethanol, and then the product was dried in the oven at 60 °C.

Synthesis of calcinated $\alpha$-Fe$_2$O$_3$ solid ellipsoid particles (CSEPs):

In a typical synthesis, The products (SEPs) were placed in the ceramic crucible and then heated to 450 °C with a heating rate of 5 °C/min. After a calcination treatment in
the air at 450 °C for 2 h, then CSEPs were obtained.

**Characterization:**

The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with CuKα radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, S4800), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F30) with an acceleration voltage of 300 kV. All TEM samples were prepared from depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. The surface areas (S) of these Fe₂O₃ particles were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. X-ray photoelectron spectroscopy (XPS) was measured on a Perkin-Elmer model PHI 5600 XPS system from a monochromatic aluminum anode X-ray source with Kα radiation (1486.6 eV), and the spectra were calibrated with the C1s peak at 284.6 eV as an internal standard.

**Gas-sensing measurement of the sample:**

The gas-sensing measurement of the as-prepared α-Fe₂O₃ sample was carried out on a WS-30A sensor measurement system (Zhengzhou Winsen Electronics Technology, China). In a typical test, a gas sensor was fabricated by coating a certain amount of α-Fe₂O₃ paste (consisting of α-Fe₂O₃ particles and the ethanol solvent) onto a ceramic tube that was previously mounted with gold electrodes and platinum conducting wires. A resistor wire coil was inserted in the tube as a heater to provide working temperatures from 200 to 500 °C by varying the heating current. The analytes were injected either directly into the chamber or, in the case of liquids like ethanol, onto a metal-plate heater in the test chamber and evaporated completely by heating. The gas-sensing capability of the sensor was defined as the ratio R_{gas}/R_{air}, where R_{gas} and R_{air} are the electrical resistance of the sensor in test gas and in air at the working temperature of about 300 °C, respectively. The α-Fe₂O₃ microcrystal-based gas-sensor was fabricated by coating the α-Fe₂O₃ powder onto the ceramic tubes of the sensor body.
Experimental Results Section:

Fig. S1 FTIR spectra of the product at the early stage of the reaction (15 min).

Fig. S2 the TGA of different reaction time of the predecessors nanoparticles at 200 °C: (a) 15 min; (b) 60 min.

According to the thermal gravimetric analysis (TGA), the total weight loss of the wire-like precursor (15 min) is about 19 % at the optimized temperature 400 °C (Fig S2a). The large weight losses further indicate that the product is amorphous phase.

The total weight loss of the precursor (60 min) in the decomposition process is about 2.8 % at the temperature 450 °C (Fig S2b), which agrees with the theoretical calculating value of 2.98 %.

2Fe_{1.833}(OH)_{0.5}O_{2.5} → 1.833Fe_2O_3 + 0.5H_2O

Theoretical calculating value = 0.5*Mr (H_2O) / 2*Mr (Fe_{1.833}(OH)_{0.5}O_{2.5})*100 % = 2.98 %.
Fig. S3 the SEM image of the calcinated SEPs to synthesize α-Fe₂O₃ solid ellipsoid particles (CSEPs) at 450 °C for 2 h.

Fig. S4 the BET of three different shape of α-Fe₂O₃ nanoparticles: (a) CSEPs; (b) HEPs; (c) HHCPs.