### Supplementary information

### 1. Experimental Section

### 1.1 Experimental materials

Poly(acrylonitrile) (PAN,  $M_w = 150\ 000$ ), poly(vinylpyrrolidone) (PVP,  $M_w = 1\ 300\ 000$ ), Tin<sub>(IV)</sub> chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) and Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) were purchased from Aldrich Chemical Co and uesd without any further purification. N,N-Dime-thylfomamide (DMF, Aldrich) was used as the solvent in the PAN and PVP solutions.

## 1.2 Fabrication of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> composite nanofibers

One dimensional electrospun  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> composite nanofibers were synthesized by simple electrospinning technique. In a typical procedure, PVP solution was prepared by mixing 0.5 g PVP and 0.4 g FeCl<sub>3</sub>·6H<sub>2</sub>O in 5 mL DMF at room temperature for 1 h with vigorous stirring. In a familiar way, PAN solution was prepared by dissolving 0.5 g PAN and 0.2 g SnCl<sub>4</sub>·5H<sub>2</sub>O in 5 mL DMF at 70 °C for 1 h with vigorous stirring. Subsequently, the PVP and PAN solutions were mixed at 70 °C for 3 h with vigorous stirring. The prepared viscous hybrid solution was then transferred into a 10 mL syringe with 19 G stainless steel needle which has a diameter of 0.7 mm. The distance between needle and static collector (aluminum foil) was maintained at 15 cm with an ac voltage of 18 kV and at a flow rate of 10 µL min<sup>-1</sup> using a syring pump (KDS LEGATO 200). Finally, the electrospun composite nanofibers were calcined at 700 °C for 2 h following a heating rate of 5 °C min<sup>-1</sup>.

To investigate how the morphology and structure of the material changing with the calcination conditions, we conducted two group experiments. Fig.S4 a and b shows the SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> composite nanofibers calcined at 600 °C and 800 °C with a heating rate of 5 °C min<sup>-1</sup>, respectively. When the calcined temperature is 600 °C, longitudinal stripes appear on the nanofibers and there are no obvious holes or porous structure. At 800 °C, the products turned out to be nanoparticles with irregular size. This may because of the excessive growth of the nanoparticles in high temperature and cannot maintain the shape of the nanowires. Fig.S4 c and d shows the SEM images of nanofibers calcined at 700 °C with a heating rate of 2 and 10 °C min<sup>-1</sup>, respectively. At a heating rate of 2 °C min<sup>-1</sup>, the nanofiber surface is smooth and no obvious boundaries can be observed. When the heating rate is 10 °C min<sup>-1</sup>, the irregular network structure can be obtained. This demonstrates that the high heating rate easily break the nanofiber structure due to the high pressure difference, which arises from the rapid decomposition and gasification of PVP and PAN.

# 1.3 Characterization of sample

X-ray power diffraction (XRD) analysis was conducted on a Rigaku TTRIII X-ray diffractometer with Cu K $\alpha$  1 radiation ( $\lambda = 1.54056$  Å) in the range of 20-70°, Field emission scanning electron microscopy (FESEM) images were recorded on a JEOL JSM-7500F microscope operating at 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-3010 microscope operated at 200 kV, respectively.



Fig.S4 FE-SEM images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> nanofibers with different calcined temperature (a and b) and heating rate (c and d).

## 1.4 Fabrication and measurement of gas sensor

Gas sensors were fabricated as follows: the as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub> composite nanofibers were mixed with water to form slurry, and then coated on an alumina tube (4 mm in length, 1.2 mm in external diameter, and 0.8 mm in internal diameter, attached with a pair of gold electrodes) by a small brush to form a thick film. The thickness of sensing films was about 100  $\mu$ m. After drying in air at room temperature, the devices were sintered at 400 °C for 2 h. A Ni-Cr alloy coil was inserted to the alumina tube as a heater allowing us to control the operating temperature of sensor. The gas response behavior of sensor was investigated under laboratory conditions (40 RH%, 23°C). The test gases were injected into a closed glass bottle by a microinjector. The gas response of sensor is defined as the ratio of the resistance of the sensor in air (R<sub>a</sub>) to that in tested gases (R<sub>g</sub>). The response time and recovery time are defined as the ratio of the time taken by the sensor to achieve 90% of the total resistance change after the sensor is exposed to the tested gas and air, respectively.