Electronic Supplementary Information

Shape-controlled Synthesis of Porous Screw-cap-like Indium Tin

Oxide and Its application for Gas Sensing

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Figure S1 The energy dispersive spectroscopy (EDS) of porous screw-cap-like ITO.

Figure S2 Schematic illustration for the structure of the gas sensor device (a) and photo of the device (b).





Figure S3 Fourier transform infrared (FTIR) spectra of (a) as-made ITO precursors (b) porous screw-cap-like ITO. The C=O stretching vibration peak is observed at 1622 cm⁻¹ on curve *a* and peaks around 1356 cm⁻¹ can be assigned to the O-C=O of the carboxylic acid group, which indicates the reaction between metal ion and carboxylic acid. After calcinations, there are no obvious peak that can be assigned to organic group on curve b due to the formation of oxide after calcinations.



Figure S4 TG and DTG curves curve for as-made screw-cap-like ITO precursor sample. TG curve shows that the total weight loss is 55.8 wt% and can divide into three processes. The first weight loss (16.6 wt.%) process from 30 to 200 °C may belong to the evaporation of the absorbed water and crystal water. The second weight loss (34.3 wt.%) and third weight loss (4.9 wt.%) occurred from 300-450 °C and 600-700°C, respectively, which may stem from the decomposition of precursor complex.



Text S1. Experimental procedure for the synthesis of porous screw-cap-like ITO.

In a typical synthesis, 0.695 g of Indium nitrate hexahydrate and 0.069 g of Tin (IV) chloride pentahydrate were dissolved in 60 mL of deionized water at room temperature with vigorous stirring for 20 min. Then 0.7 g of trisodium citrate dihydrate was added to the solution, and stirring for 10 min. After forming citrate complexes, 0.38 g of oxalic acid dihydrate was added and then stirred for 20 min. Further adding 20 mL of deionized water and the solution was sealed and kept unstirred at room temperature for 24 h. The obtained precipitate was collected after being washed several times with deionized water and dried at 80 °C. To get porous screw-cap-like ITO, the as-made ITO precursors were calcined in a muffle furnace at 700 °C for 2h.

For the preparation of the gas sensor devices, porous screw-cap-like ITO particles were mixed and ground with terpineol to form a paste, and then coated onto a ceramic tube substrate with Au wire as electrodes. The samples were subsequently dried at 100 °C and calcined at 400 °C for 2 h to remove organic paste. Then, a heater strip was placed through the tube to provide the working temperature of the gas sensor.

The sensor was kept around 330 °C aging for 1 week before gas sensitive measurement. In measuring the electric circuit for gas sensors, a load resistor was connected in the series with the gas sensor. The circuit voltage was fixed at 5 V, and the output voltage (V_{out}) was the terminal voltage of the load resistor. The working temperature of the sensor was adjusted through varying the heating voltage. The resistance of the sensor in air or targeting gas was measured by monitoring the V_{out} . The test was operated in a measuring system of HW-30A (Hanwei Electronics Co. Ltd., PR China). Targeting gas was injected into a test chamber with different concentrations and the time-dependant changes on V_{out} were recorded. After several steps of injection, the targeting gas was quickly removed, and the recovery curve was recorded.

The structure of porous screw-cap crystals was examined by large angle X-ray diffraction (XRD), using German Bruker D4 X-ray diffractometer with Ni-filtered Cu K α radiation (40 kV, 35 mA). The photo microscopy images were recorded by Leica DM 2500M microscopy. The morphologies of ITO and precursors were investigated by using field-emission scanning electron microscopy (SEM), equipped with energy-dispersive spectroscopy (EDS) analyzer. The samples were sputter-coated with platinum before the analysis, and the accelerating voltage for the Everhart-Thornley detector (ETD, routine imaging) is 5kV and for through-the-lens detector (TLD, high magnification/resolution imaging) is 15 kV, respectively. Nitrogen sorption isotherms were measured at 77 K with a Micromerites Tristar 3000 analyzer. Before measurements, the samples were degassed in vacuum at 200 °C for at least 6 h. Thermogravimetry analysis (TGA) was carried out using a Mettler Toledo TGA-SDTA851 analyzer from 25 to 800 °C under nitrogen with a heating rate of 10 °C/min. Fourier transform infrared (FTIR) spectra were collected from Nicolet Fourier spectrophotometer.