

Template-free preparation of mesoporous single crystal In₂O₃

achieving superior ethanol gas-sensing performance

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Experiments

All of the reagents, indium chloride tetrahydrate (InCl₃·4H₂O, A.R), aqueous ammonia (NH₃·H₂O, 25-28%) and hydrochloric acid (HCl, 36-38%) were used as received without any further purification. Deionized water was used throughout the experiments.

In a typical synthesis of MSC In₂O₃ particle, InCl₃·4H₂O (0.293 g, 1 mmol) were added to deionized water (35 ml) to form a solution. Under magnetic stirring, aqueous ammonia and hydrochloric acid was used to adjust the pH value of the solution as 11. The reactive solution was put into a Teflon-lined autoclave of 50 ml capacity. The autoclave was sealed and heated at 180 °C for 24 h. Then, the autoclave was allowed to cool to room emperature naturally. The resulting white products In(OH)₃ precursor were dried for 4 h at 80 °C, then annealed at 300 °C for 2h to obtain the MSC In₂O₃ product. For the synthesis of M In₂O₃ particle, the pH value of the reactive solution was changed to 9, while other reaction conditions were unvaried.

Characterization

X-ray powder diffraction (XRD) analysis were conducted on a TD-3500 X-ray diffractometer with Cu Kα1 radiation (λ=1.54056 Å). Scanning electron microscopy (SEM) images were recorded on a FEI INSPECT S 50 microscope operating at 25 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by employing a FEI Tecnai G2 S-Twin transmission electron microscope with a field-emission gun operating at 200 kV. Fourier transform infrared spectroscopy (FTIR) were recorded on a Bruker VERTEX 70 FT-IR spectrometer. Particle size distribution of sample were measured on Zetasizer Nano ZS 90. XPS measurements were performed on a PHI 5700 XPS/ESCA system with a monochromatic Al Kα (1486.6 eV). All binding energies were calibrated to C1s peak at 284.6 eV of the surface adventitious carbon. Thermogravimetry-Differential Scanning Calorimetry (TG-DSC) was performed using a Netzsch STA 499 F1 Juptier in flowing Ar gas at a heating rate of 10 °C·min⁻¹. The surface areas of the two types of In₂O₃ samples with different pore size were measured by the BET method by measuring nitrogen-adsorption and desorption isotherms on an AUTOSORB-1 Surface Area and Pore Size Analyzer.

Gas Sensor Fabrication and Measurement

The gas sensors were fabricated and measured as follows: The gas sensors were fabricated by coating the slurry of MSC/M In₂O₃ powders onto the ceramic tube

without an additional annealing process. Then an alloy coil through the tube was employed as a heater to control the operating temperature. The electrical contact was made through connecting the four platinum wires on the ceramic tube with the socket by gold paste. Typically, the gas sensors were placed in a chamber and the gas-sensing experiments were conducted under a laboratory conditions. The response of the sensor was defined as $S=R_a/R_g$, where R_a and R_g were the resistances of the sensor in the air and target gas, respectively. The response and recovery times are defined as the time taken by the sensor to achieve 90 % of the total resistance change during adsorption and desorption process, respectively.

Experimental Results Section:

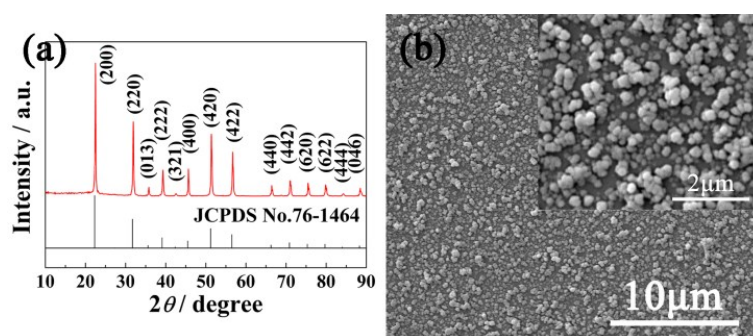


Fig. S1 Crystal structure and morphology of MSC $\text{In}(\text{OH})_3$ precursors: (a) XRD and (b) SEM.

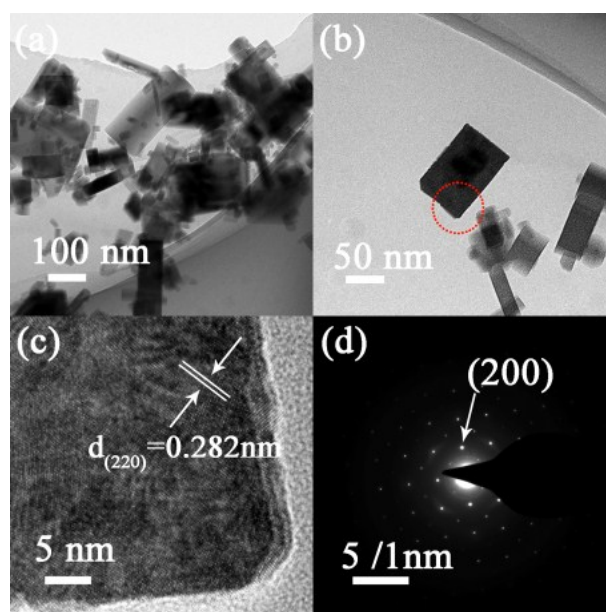


Fig. S2 Electron microscopy images of MSC $\text{In}(\text{OH})_3$ precursor: (a) low-magnification TEM, (b) high-magnification TEM (c) HRTEM and (d) SAED.

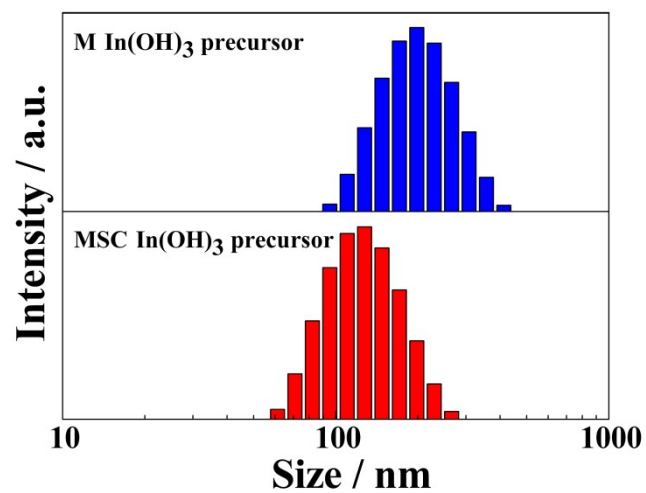


Fig. S3 Size distribution histograms of MSC and M In(OH)₃ precursors.

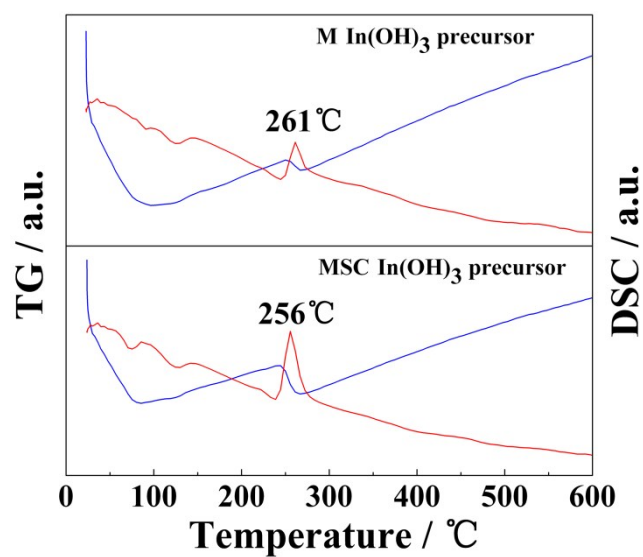


Fig. S4 TG-DSC curves of MSC and M In(OH)₃ precursor.

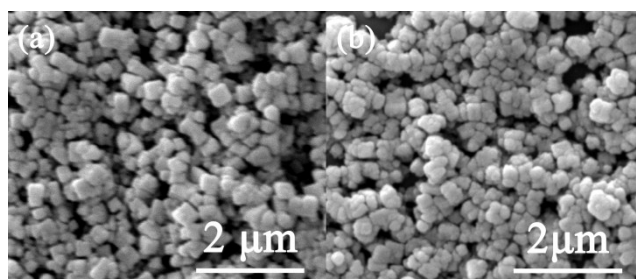


Fig. S5 SEM images of (a) M In(OH)₃ precursor and (b) M In₂O₃ product.

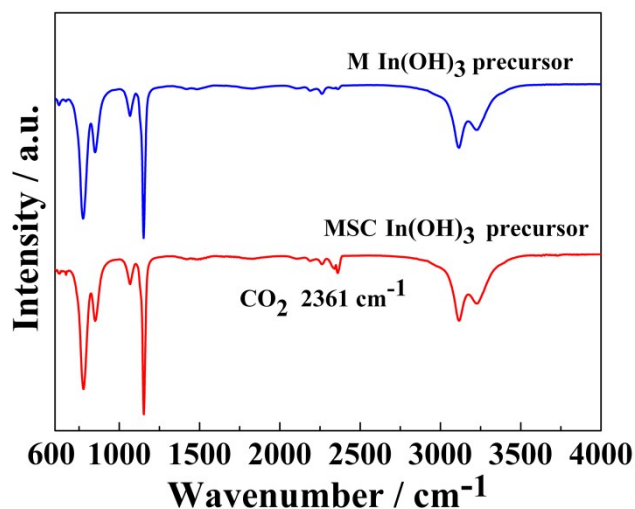


Fig. S6 FTIR spectra of MSC and M In(OH)₃ precursor. Lower frequencies of ~700 cm⁻¹ are typical of In-O-In symmetric and asymmetric stretches. The intense bands at 1210 and 1080cm⁻¹ are the deformation vibration of the -OH group. The absorption bands at ~3300 cm⁻¹ are attributed to the O-H stretch. The intense bands at 2361 and 2339 cm⁻¹ are the asymmetric stretching mode of CO₂ molecules.

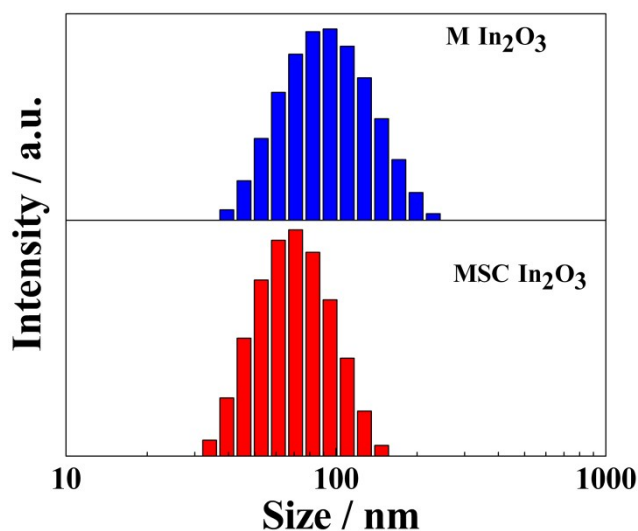


Fig. S7 Size distribution histograms of MSC and M In₂O₃ particles.

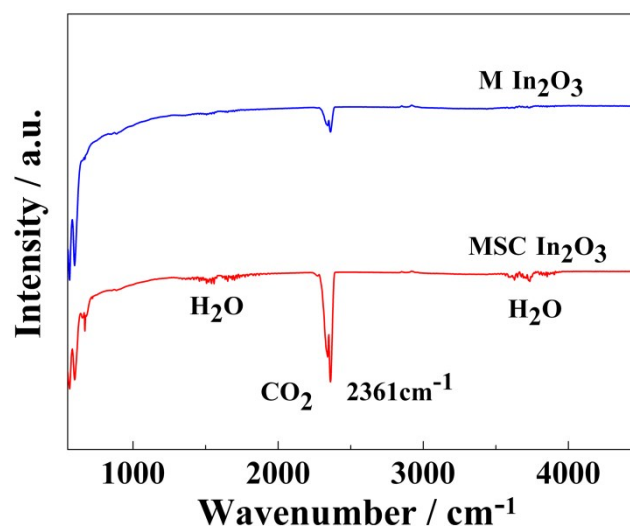


Fig. S8 FTIR spectra of MSC and M In₂O₃ particles. The band around 500 cm⁻¹ is attributed to the In-O vibration absorption. The intense bands at 2361 cm⁻¹ and 2339 cm⁻¹ are the asymmetric stretching mode of CO₂ molecules. The intense bands at 1300-2000 cm⁻¹ and 3400-4000 cm⁻¹ are stretch and bend vibration absorption of H₂O molecule.

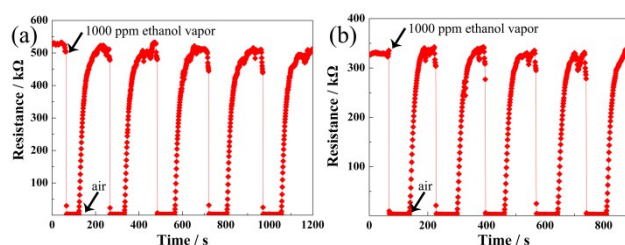


Fig. S9 Resistance response of (a) MSC and (b) M In₂O₃ particles to 1000 ppm ethanol gas at 225 °C.