Electronic supplementary information

Three-dimensional ordered macroporous In_2O_3-supported Au for high-performance ethanol sensing

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1. Materials preparation

The regularly arrayed PMMA microspheres with an average diameter of ca. 300 nm (Figure S1) were synthesized according to the method reported in the literature [1-2].

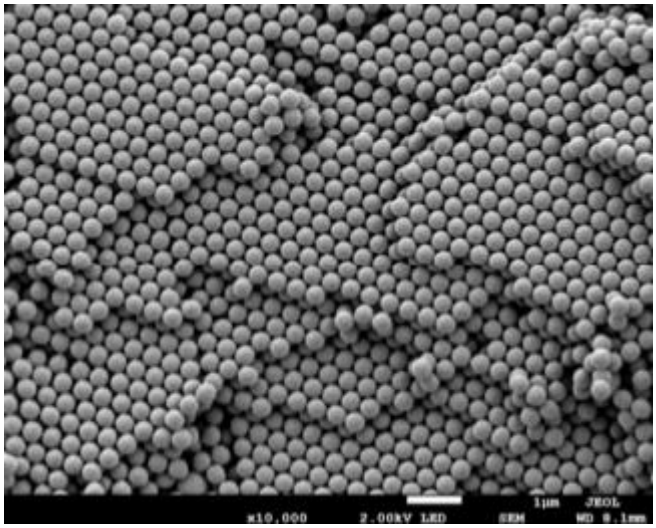

Fig. S1 SEM images of PMMA templates.

3DOM In_2O_3 were prepared using a surfactant-assisted PMMA colloidal crystal template method. In a typical procedure, a stoichiometric amount of $In(NO_3)_3 \cdot 4.5H_2O$ was dissolved in 10 mL of methanol at room temperature (RT) with stirring for 1 h to obtain a transparent solution. Then 4.5 g citric acid was added into the metal nitrate-containing transparent solution with stirring for 1 h to obtain a precursor solution. 2.0 g PMMA microspheres were soaked in the precursor solution for 4 h. The PMMA microspheres were filtered and dried in air at RT for 48 h, and then transferred to a ceramic boat. The calcination process included two steps: firstly, the obtained sample was calcined in N_2 (60 mL/min) from RT to 300 ^oC (1 ^oC/min) and kept at 300 ^oC for 3 h, and then cooled to 50 ^oC. Secondly, the sample was heated in air from RT to 300 ^oC (1 ^oC/min) and maintained at 300 ^oC for 3 h, and then was calcined at the same ramp from 300 to 600 ^oC and held at 600 ^oC for 3 h. After cooling to RT, 3DOM In_2O_3 was obtained.

Au-3DOM In_2O_3 nanocomposites were prepared via in situ $NaBH_4$ reduction method. The typical preparation procedure is as follows: 200 mg 3DOM In_2O_3 was dispersed in aqueous solution and 522.6 μL $HAuCl_4$ (4 g/L) was added at RT with stirring. Then, 0.01 mol/L $NaBH_4$ was injected with stirring for 30 min. After being filtered, the obtained products were dried at RT for 48 h.

2. Material characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker/AXS D8 Advance X-ray diffractometer operated at 40 kV and 35 mA with a Cu *K*〈 X-ray irradiation source (⎣ = 0.15406 nm). The investigation by means of scanning electron

microscope (SEM) was conducted on an S-4700 apparatus operated at 10 kV. Transmission electron microscopic (TEM) and high-resolution TEM images of the samples were obtained using a JEOL JEM-2010 instrument. The X-ray photoelectron spectroscopy (XPS) was used to determine the gold and indium species, respectively, with Al Kα (hv=1486.6 eV) as the excitation source. The C 1s signal at BE = 284.6 eV was taken as a reference for BE calibration. Au content of the sample was determined by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7700).

3. Sensor fabrication and gas-sensing measurements

The sensors were fabricated using the as-prepared Au-3DOM In_2O_3 as the building blocks and the detailed fabrication were as follows. A predetermined amount of Au-3DOM In_2O_3 was ground together with ethanol. The formed slurry was coated on an alumina tube with a pair of Au electrodes and four Pt wires on both ends of the tube, and aged at 300 °C for 24 h. A Ni-Cr wire coil throughout the tube was employed as a heater to control the working temperature by tuning the heating voltage. Gas sensing tests were performed on a WS-30A gas sensing measurement system (Weisheng Electronics Co., Ltd., Henan Province, China). The scheme and working principle of SW-30A gas sensing measurement system are analogical as showed by our previous reports [3-5]. The response (R) is defined as Ra/Rg, where Ra and Rg are the resistance of the sensor in air and in test gas, respectively. The time spent by the sensor on achieving 90% of the total resistance change is defined as the response time in case of adsorption or as the recovery time in case of desorption.

4. Temperature-programmed surface reaction (TPSR)

50 mg Au-3DOM In_2O_3 were packed into a quartz tube reactor. The reaction stream was created by flowing He at 50 mL/min through an ethanol bubbler. This stream was mixed with 5% O_2/He flowing at 25 mL/min to produce a reaction mixture. During TPSR, the temperature was swept to 500 ^oC (5 ^oC/min). The output gas was analyzed continuously using online mass spectrometer (RGA, Standford Research Systems QMS-100).Because the reactant ethanol and observed products had considerable overlap in mass peaks, in order to distinguish the products in the output gases, some products were represented by other fragment mass, such as 29 represents CH_3CHO. The gases included CH_3CH_2OH (31), H_2O (18), O_2 (32), CH_3CHO (29), H_2 (2), CO_2 (44), CO (28), $CH_3COOCH_2CH_3$ (43).

5. Results

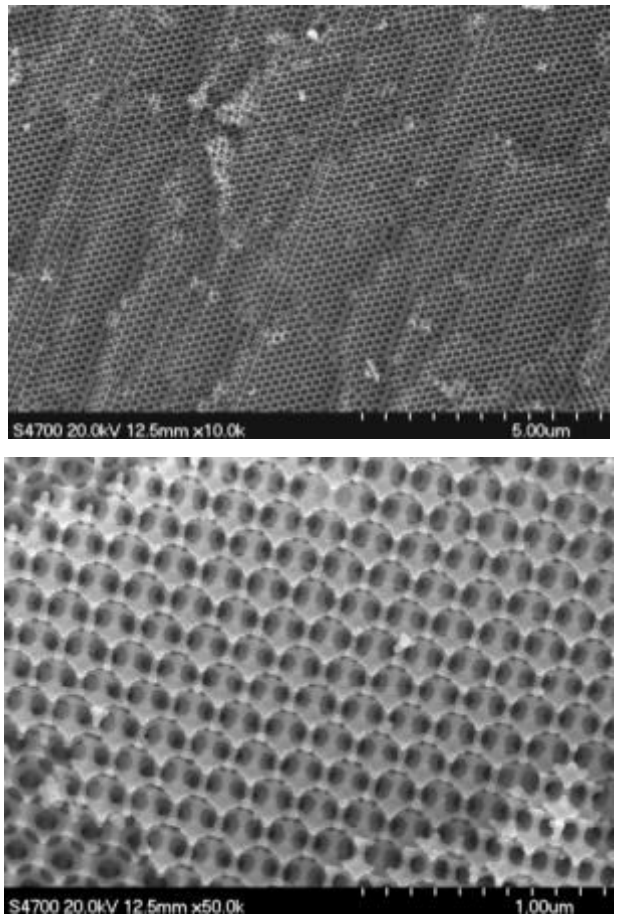

Fig. S2 SEM images of 3DOM In_2O_3 with different magnifications.

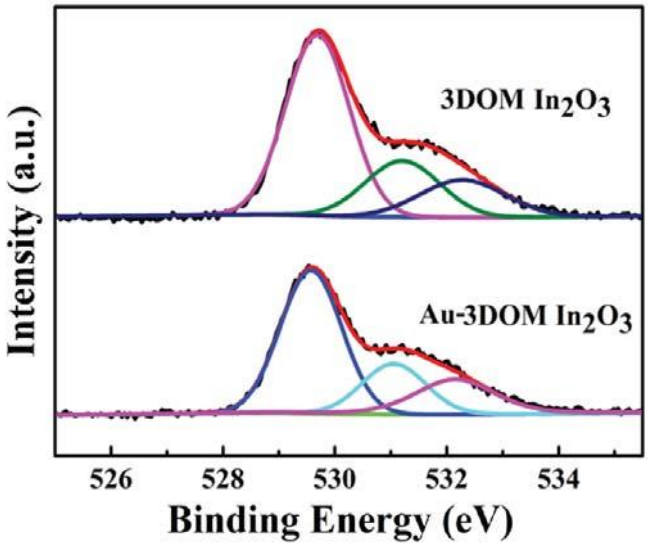

Fig. S3 O1s XPS spectra of 3DOM In_2O_3 and Au-3DOM In_2O_3

Table S1 Contents of oxygen species of 3DOM In_2O_3 and Au-3DOM In_2O_3

Species	3DOM In_2O_3		Au-3DOM In_2O_3	
	Peak (eV)	Percentage (%)	Peak (eV)	Percentage (%)
O_I	529.65	49.74	529.79	49.19
O_{II}	531.02	17.82	531.38	18.48
O_{III}	532.20	32.44	532.47	32.33

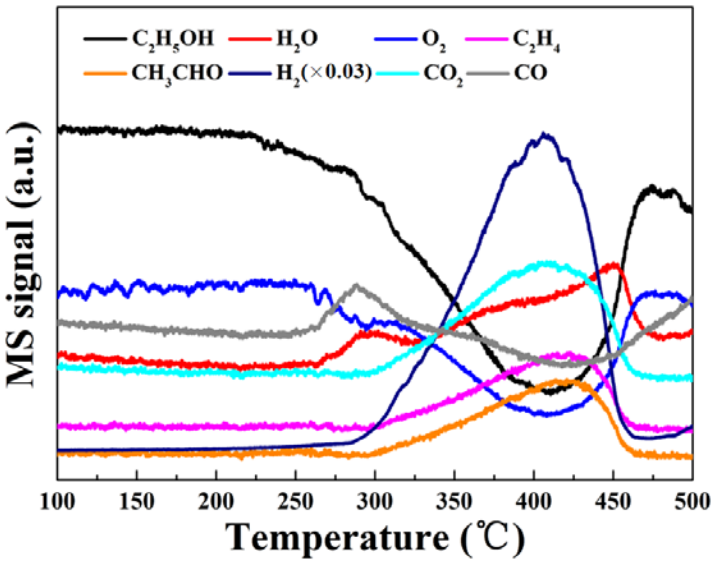

Fig. S4 TPSR curves of 3DOM In_2O_3.

References

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