

## Supporting Information

### Fabrication and measurement of sensors

#### Fabrication and Characterization of Sensing Nanospheres.

The Ti precursor solutions were prepared by dissolving 0.9 g TiCl<sub>4</sub> (Aldrich) in 0.2 mol ethanol in the presence of 2E-5 mol PluronicF127 triblock copolymer [(HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>106</sub>-(CH<sub>2</sub>CH(CH<sub>3</sub>)O)<sub>70</sub>-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>106</sub>H, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>], Sigma). For Pt doping, 0.04g PtCl<sub>4</sub> (Aldrich) was dissolved in 0.5 ml 12 M HCl and then mixed with the above Ti precursor solution under constant stirring for two days. The resulting (clear) Pt-Ti precursor solutions were stable over a one month period. The molar ratio of TiCl<sub>4</sub>:F127:EtOH:PtCl<sub>4</sub>:HCl:H<sub>2</sub>O in the final Pt-Ti precursor solution was 1:0.01:40:0.02:3:10. Gas sensing nanospheres were prepared on the sensor device of ca. 10 × 10 mm<sup>2</sup> with interdigital electrode. In brief, a cleaned sensor device was first placed on the petri dish and subsequently covered with the above sol solution on the surface of the sensor device (about 0.5 mm in thickness); second, the gel was formed on the sensor device after liquid evaporation under 30% relative humidity. The sensor device with gel was put in a vessel with 90% relative humidity, and then the vessel was sealed and put into the oven with the temperature at 100°C for 72h. The as-fabricated nanospheres were then heat treated by annealing at temperatures of 200, 300, 400 and 400°C for 2 h with an up/down ramp rate of 1.0°C/min.

WAXRD data were obtained by a Bruker D8 Advance X-ray diffractometer with Cu Kα (0.15406 nm) radiation. Nitrogen sorption measurements were carried out at 77 K using a NOVA 4000e (Quantachrome Instruments) on Pt decorated titania scratched from several films. High resolution transmission electron microscopy (HRTEM) was performed using a FEI Titan 80-300 equipped with a field emission gun operated at 300 kV; nanospheres were scratched from the substrate and collected on an amorphous holey carbon film on a copper grid. XPS spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source (hν= 1486.6 eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). Surface charging was corrected by referencing the spectra to C-C state of the C 1s peak at binding energy at 284.6 eV. All XPS spectra were recorded using an aperture slot of 300\*700 microns, survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV. Raman spectra were recorded with a LabRAM HR UV-vis (Horiba Jobin Yvon) Raman microscope (Olympus BX41) with a Symphony CCD detection system using a HeNe laser at 632.8 nm. The spectra were taken from material removed from the substrate.

#### Gas-Sensing Measurement

During the sensing measurement, liquid VOCs were inputted through a sample inlet and led down to a heater, which vaporized it. A fan ensured that the vapour was homogeneously distributed. The gas sensing properties were determined in a sample cell consists of a sample chamber and has a gas inlet and outlet. Resistance changes upon sample exposure to gases were recorded by a high resistance meter Keithley 6517B. The sensor response is defined as  $S = (R_a - R_g)/R_g$  or  $S = (R_g - R_a)/R_a$ , where  $R_a$  and  $R_g$  are the sensor resistances in air and in the target gas, respectively.

This parameter is positive (negative) for n-type (p-type) ethanol (benzene) sensing. Here, the response or recovery time is defined as the time taken for the sensor to achieve 90% of its maximum response or decreases to 10% of its maximum response, respectively.

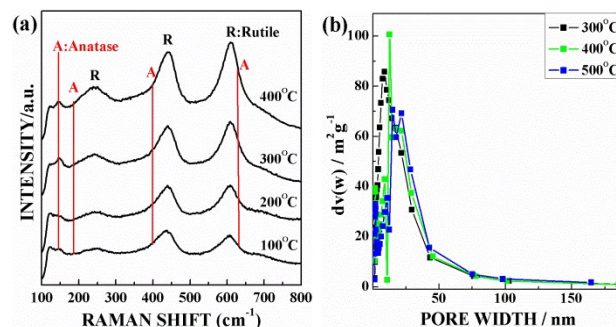


Fig. S1 (a) Raman spectrum of as-synthesized nanospheres and Pt-TiO<sub>2</sub> nanospheres annealed at 200°C, 300°C, 400°C, and 500°C. (b) corresponding pore-size distribution for Pt-TiO<sub>2</sub> nanospheres annealed at 300°C, 400°C, and 500°C.

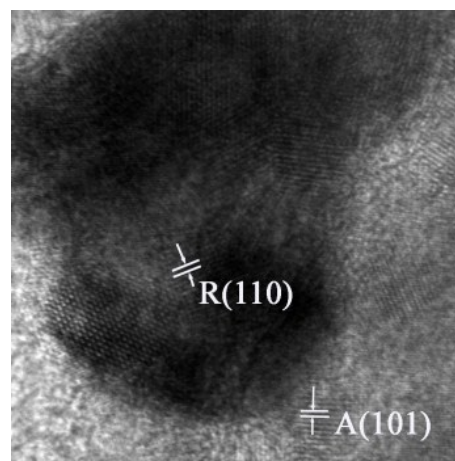


Fig. S2 HRTEM image of the 300°C calcined hierarchical nanosphere.

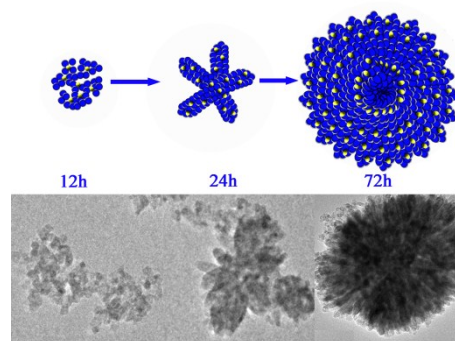
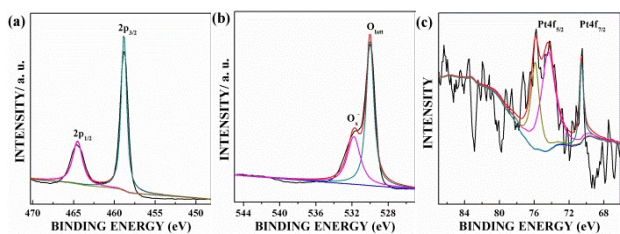
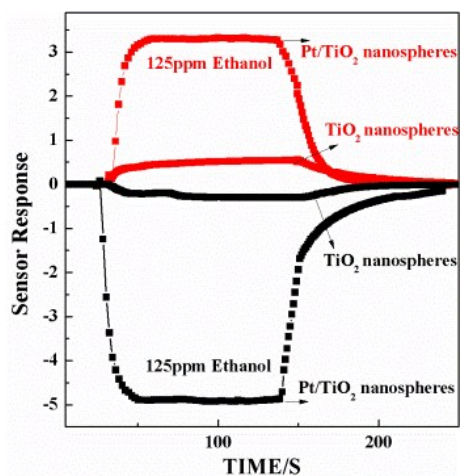


Fig. S3 Schematic illustration of the growing process of hierarchical TiO<sub>2</sub> nanospheres. TEM images of 12h, 24h, and 72h psHT treated titania with 300°C calcination.



**Fig. S4** (a) Ti 2p, (b) O1s and (c) Pt 4f spectra of the 300°C annealed Pt-TiO<sub>2</sub> nanospheres.



**Fig. S5** Response curves of Pt/TiO<sub>2</sub> nanospheres and TiO<sub>2</sub> nanospheres to 125ppm ethanol and benzene at room temperature.

**Table S1.** TiO<sub>2</sub>-based VOCs gas sensors reported before and in this work.

Sensing materials	VOCs concentration	Operating temperature	Response value
This work	125 ppm	RT	4.9
anatase/rutile nanotubes	5000 ppm	200 °C	3.5
nanoporous TiO <sub>2</sub> films	/	75 °C	<0.25
TiO <sub>2</sub> films	150 ppm	RT	<0.1
GaN/TiO <sub>2</sub> nanocluster	150 ppm	RT	<0.3