Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information for:

Fabrication of Tin Dioxide Nanowires with Ultrahigh Gas Sensitivity by Atomic Layer Deposition of Platinum

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Experimental

a. Preparation of SnO_2 nanowires

The single-crystal SnO_2 nanowires were synthesized on an alumina substrate by thermal evaporation with high purity Sn powders (0.4 g, Aldrich, 99.99%) used as the evaporation precursors in an alumina boat. Before synthesizing the SnO_2 nanowires,a 5 nm Au film coated on to an alumina substrate was served as the catalyst, which indicates that the growth of the single-crystal SnO_2 nanowires follows a catalyst-assisted vapor-liquid-solid (VLS) mechanism.[1] The temperature of the system was raised to 950 °C at 20 °C /min with Ar at a fixed flow rate of 10 sccm, kept at that temperature (950 °C) for 1 h under a mixed gas of 10 sccm Ar and 4 sccm O_2, and then cooled to room temperature without any O_2 being introduced. During the growth, the pressure of the quartz tube was maintained at 1 Torr.

b. Morphology, crystal structure and chemical composition of SnO_2 nanowires

The morphology, crystal structure and chemical composition of the SnO_2 nanowires were characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-6500F), a MAC glancing incident *x*-ray diffraction spectrometer, and *x*-ray photoelectron spectroscopy (XPS Perkin–Elmer Model PHI1600 system) using a single Mg-K_α (1253.6eV) x-ray sources operated at 250 W. Energy calibration was conducted using the Au $4f_{7/2}$ peak at 83.8 eV, and the energy resolution was 0.2 eV for the core-level spectra. The binding energy (BE) scales have been referenced to the C 1s orbital at 285.0 eV, arising from the carbon contamination on the surface of the samples.

Results

a. XPS analysis of pristine SnO2 nanowires

In Figure S2a, the Sn 3d core-level spectrum includes two peaks: Sn $3d_{3/2}$ peak at 495.7 eV is ascribed to Sn^{4+}, whereas the Sn $3d_{5/2}$ peak at 487.1 eV is ascribed to Sn^{2+} and Sn^{0}. Figure S2b is the O 1s core-level spectrum, which can be deconvoluted into two peaks assigned to Sn-O (530.7 eV) and O-H (532.5 eV). This indicates that the nanowires consist of a mixture of Sn^{0}, Sn^{2+} and Sn^{4+}.[2, 3] The O-H peak resulting from the H_2O species present as a residue on the alumina substrate or from the quartz tube during the thermal evaporation, and the dissociated H_2O molecules can be absorbed on to an oxygen bridging vacancy to form hydroxyl groups, which are subsequently incorporated into the nanowires during crystal growth.[4-6] Consequently, there are a large amount of OH groups on SnO_2 nanowire surface.

b. The analysis of the lattice spacings and angles between reflections

From the XRD analysis, SnO_2 nanowires have the tetragonal rutile crystal structure with the lattice constants, $a = b = 4.738$ Å, and $c = 3.188$ Å, which is consistent with the single crystal SnO_2. Furthermore, based on the theory of crystallography, the angle θ between two planes in a tetragonal system with Miller indices $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is given by

$$\cos\theta = \frac{\frac{h_1h_2 + k_1k_2}{a^2} + \frac{l_1l_2}{c^2}}{\left(\frac{h_1^2 + k_1^2}{a^2} + \frac{l_1^2}{c^2}\right)^{1/2}\left(\frac{h_2^2 + k_2^2}{a^2} + \frac{l_2^2}{c^2}\right)^{1/2}} \qquad (1)$$

So the angle between the (101) plane and (200) is calculated to be about 56°, and the angle between the (101) plane and $(10\bar{1})$ is calculated to be 112°, which is in good agreement with SAED pattern.

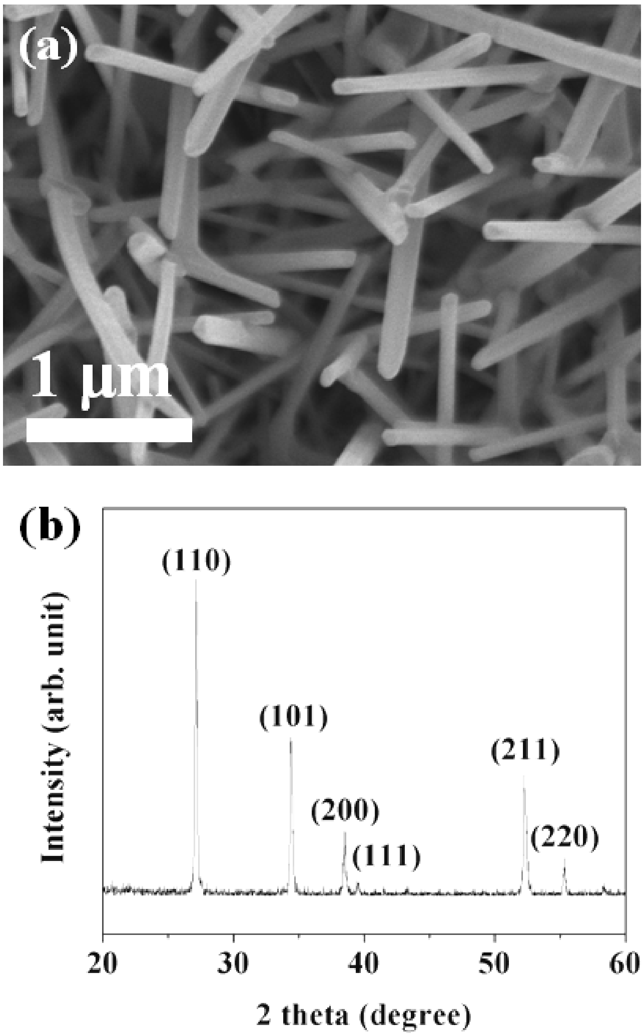

Figure S1 (a) FESEM image and (b) *x*-ray diffraction pattern of SnO_2 nanowires synthesized by thermal evaporation.

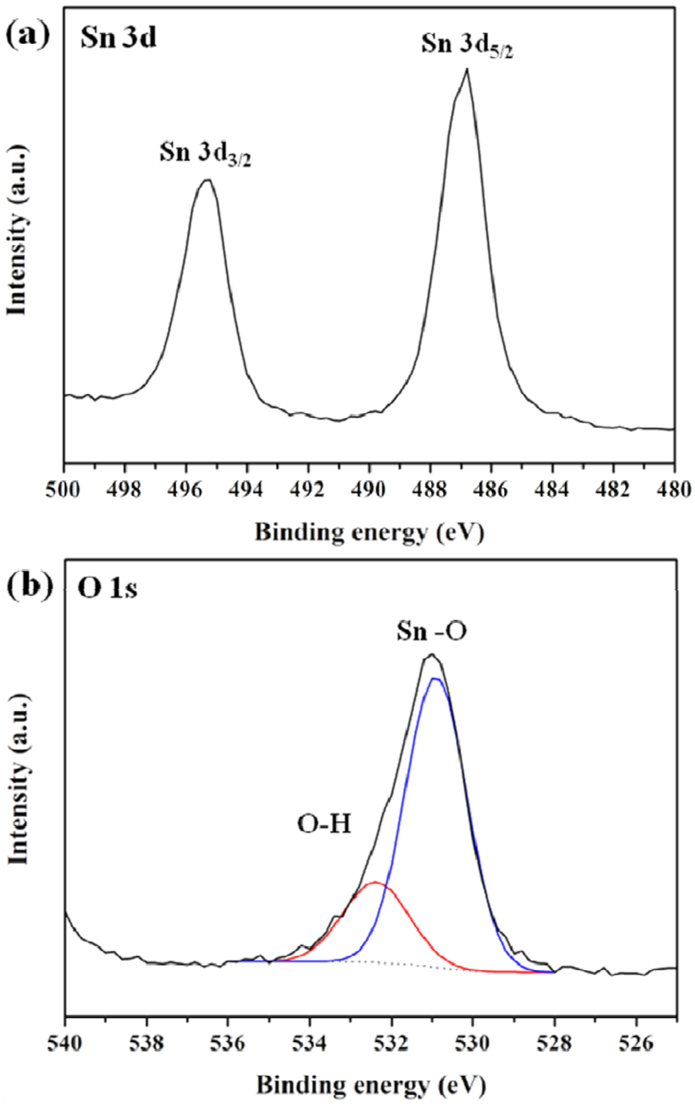

Figure S2 (a) Sn 3d and (b) O 1s XPS core-level spectra of SnO_2 nanowires synthesized by thermal evaporation.

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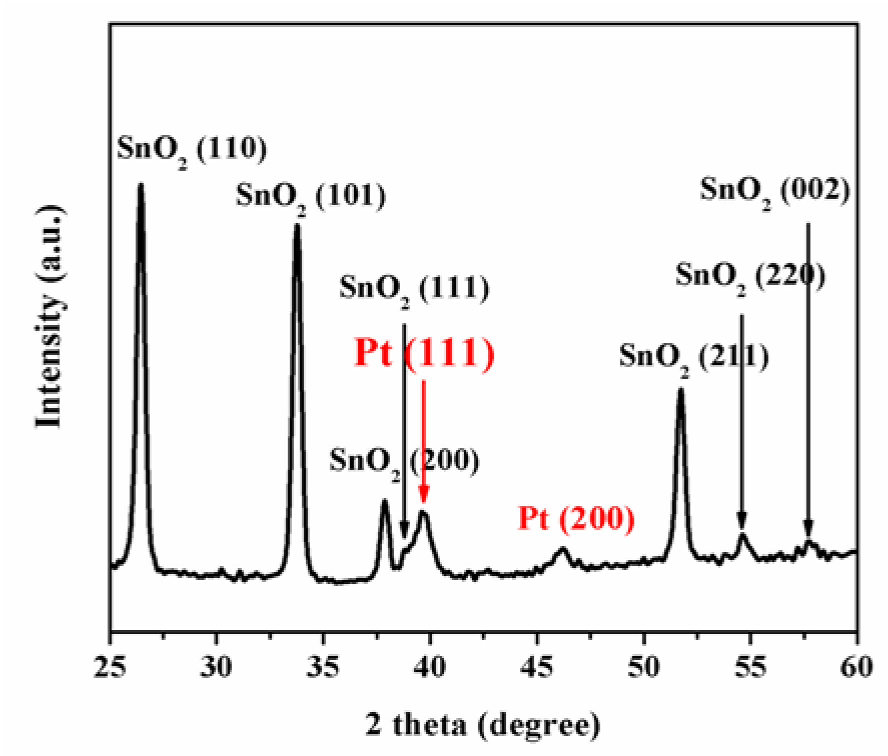

Figure S3 A *x*-ray diffraction pattern of Pt-decorated SnO_2 nanowires, showing that the ALD of Pt nanoparticles having FCC structure.

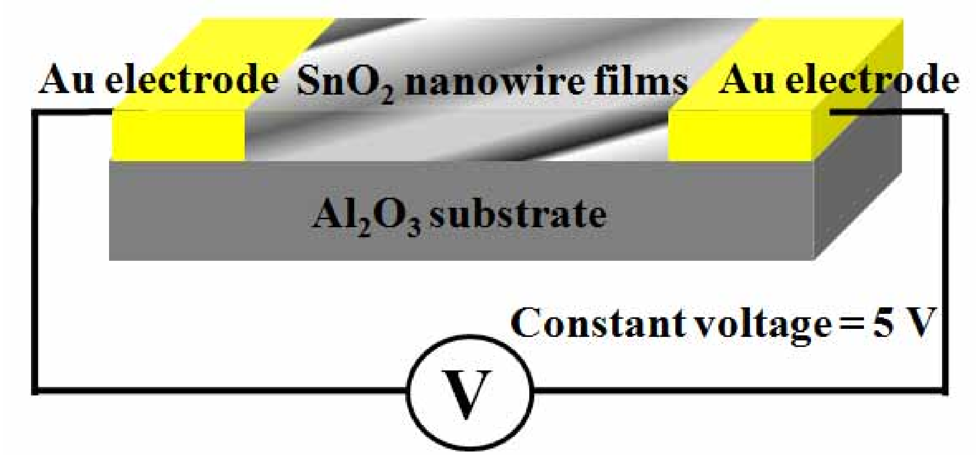

Figure S4 Schematic picture of the SnO_2 nanowire-based gas sensors.

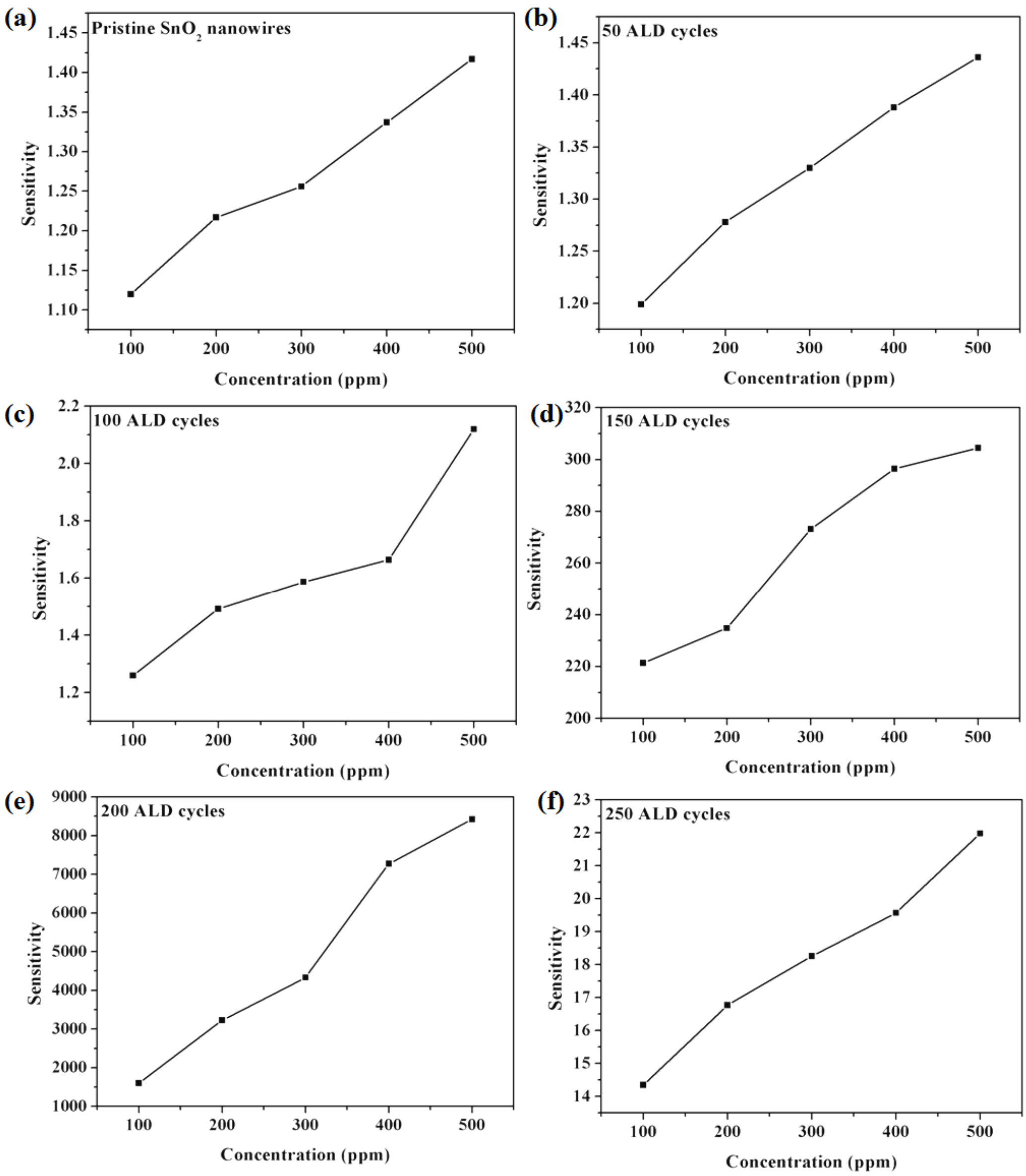

Figure S5 Gas sensitivity of the gas sensors tested for 100-500 ppm ethanol vapor at 200 °C fabricated from the (a) pristine SnO_2 nanowires, and after ALD of Pt for (b) 50 , (c) 100, (d) 150, (e) 200, and (f) 250 cycles.

References

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