

Supporting Information

A Solution-Phase, Precursor Route to Polycrystalline SnO₂ Nanowires That Can Be Used for Gas Sensing under Ambient Conditions

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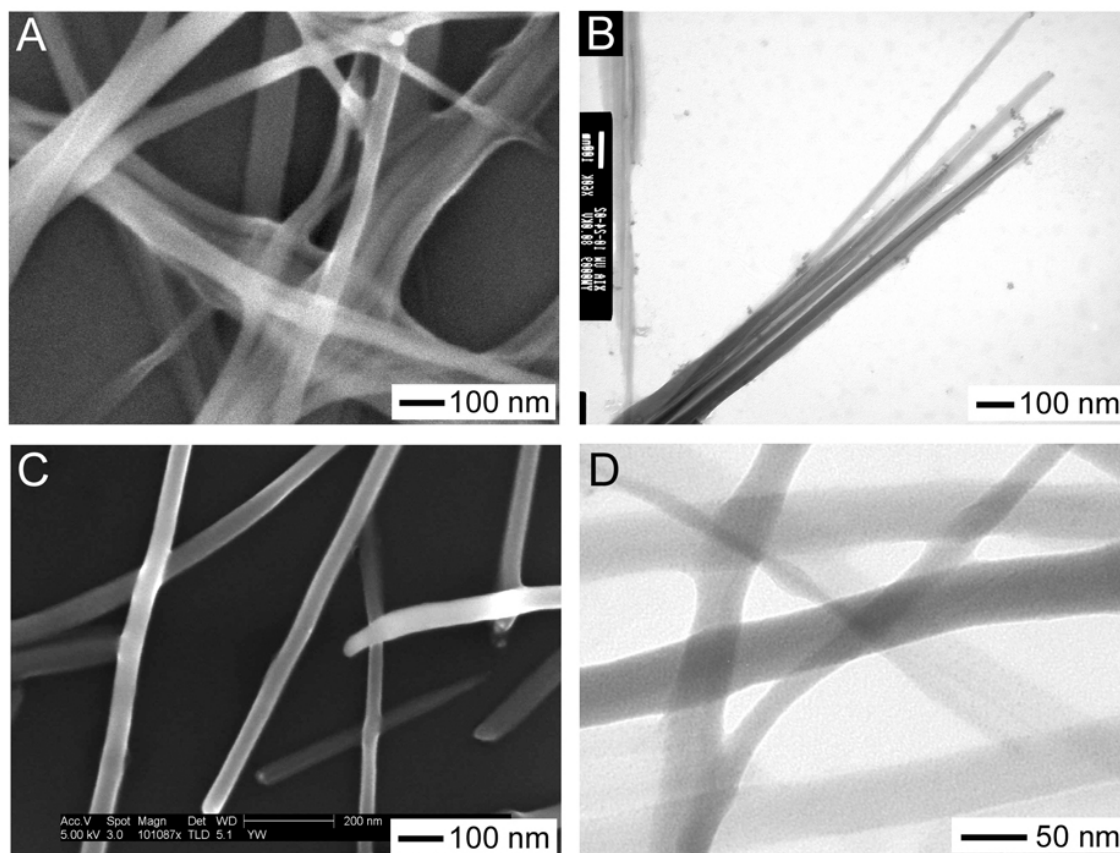


Figure S1. (A, B) High-magnification SEM and TEM images of the precursor nanowires showing the formation of bundles. (C, D) High-magnification SEM and TEM images of the precursor nanowires showing the formation of a smooth surface on each wire and a densely packed structure in each wire, respectively.

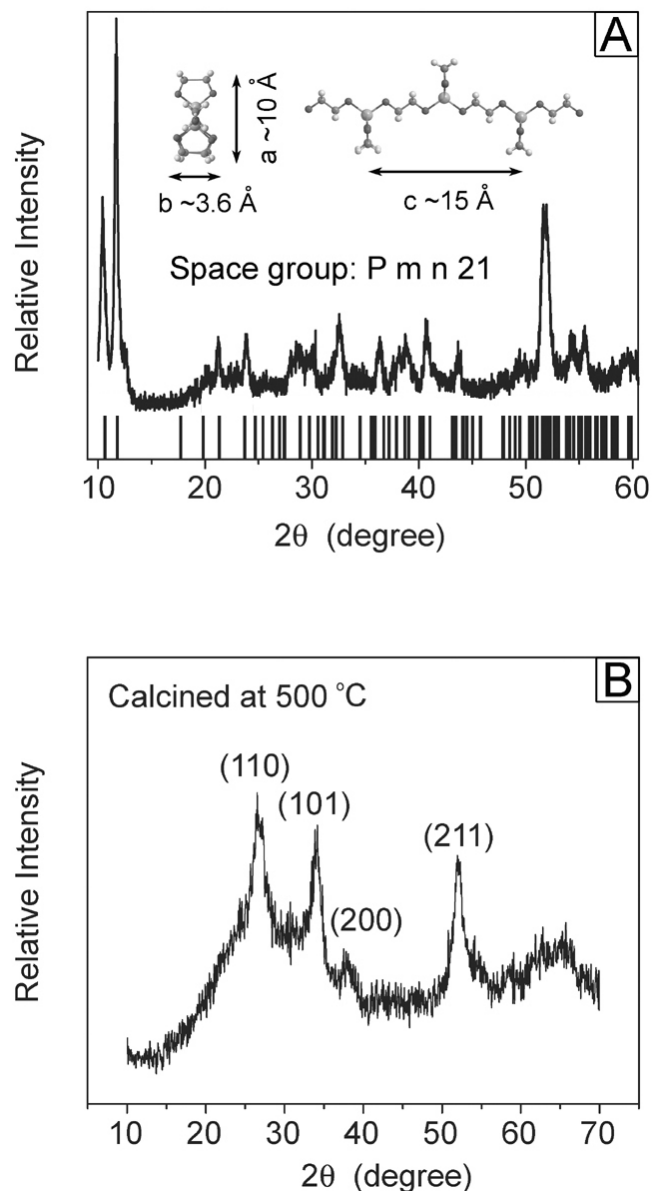


Figure S2. (A) Comparison between the experimental XRD pattern and the calculated peak positions (vertical bars at the bottom) for the nanowires before calcination. The inset shows drawings of the structures and approximate dimensions of each repeating unit derived using the CHEM 3D® model. (B) XRD pattern taken from a calcined sample indicating the conversion of the precursor compound into rutile-phased SnO₂. Based on the Scherrer's formula, a crystallite size of 3-7 nm was estimated from the peak widths, and this value agreed well with the results of TEM observation.

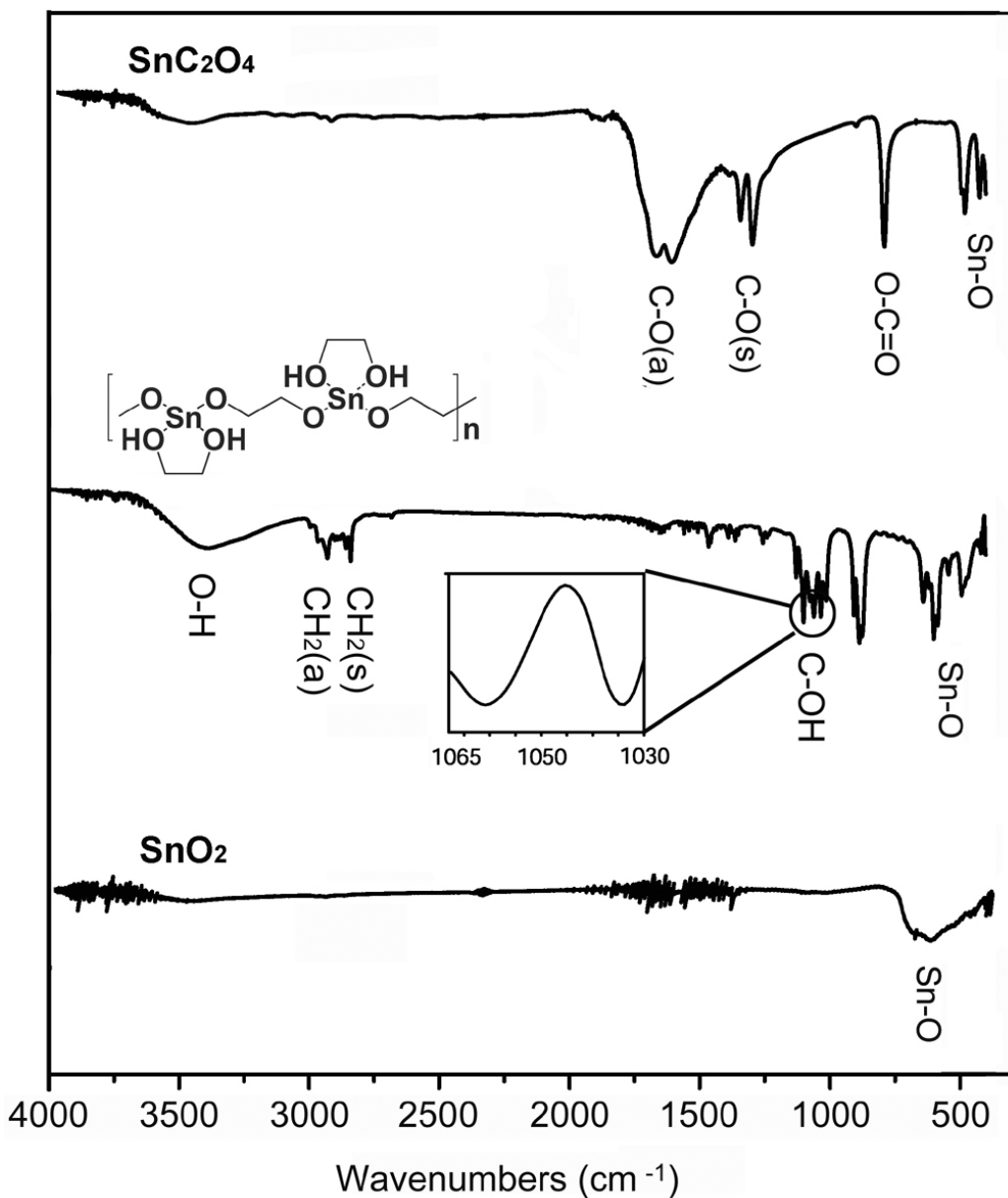


Figure S3. FT-IR spectra taken from KBr pellets that contained the starting material (SnC_2O_4), the precursor nanowires, and the nanowires (made of SnO_2) after calcination. For the precursor nanowires, a magnified view (inset) of the region corresponding to C-O vibrations was also given. For all measurements, the dried samples were mixed with KBr powders and then compressed into pellets.

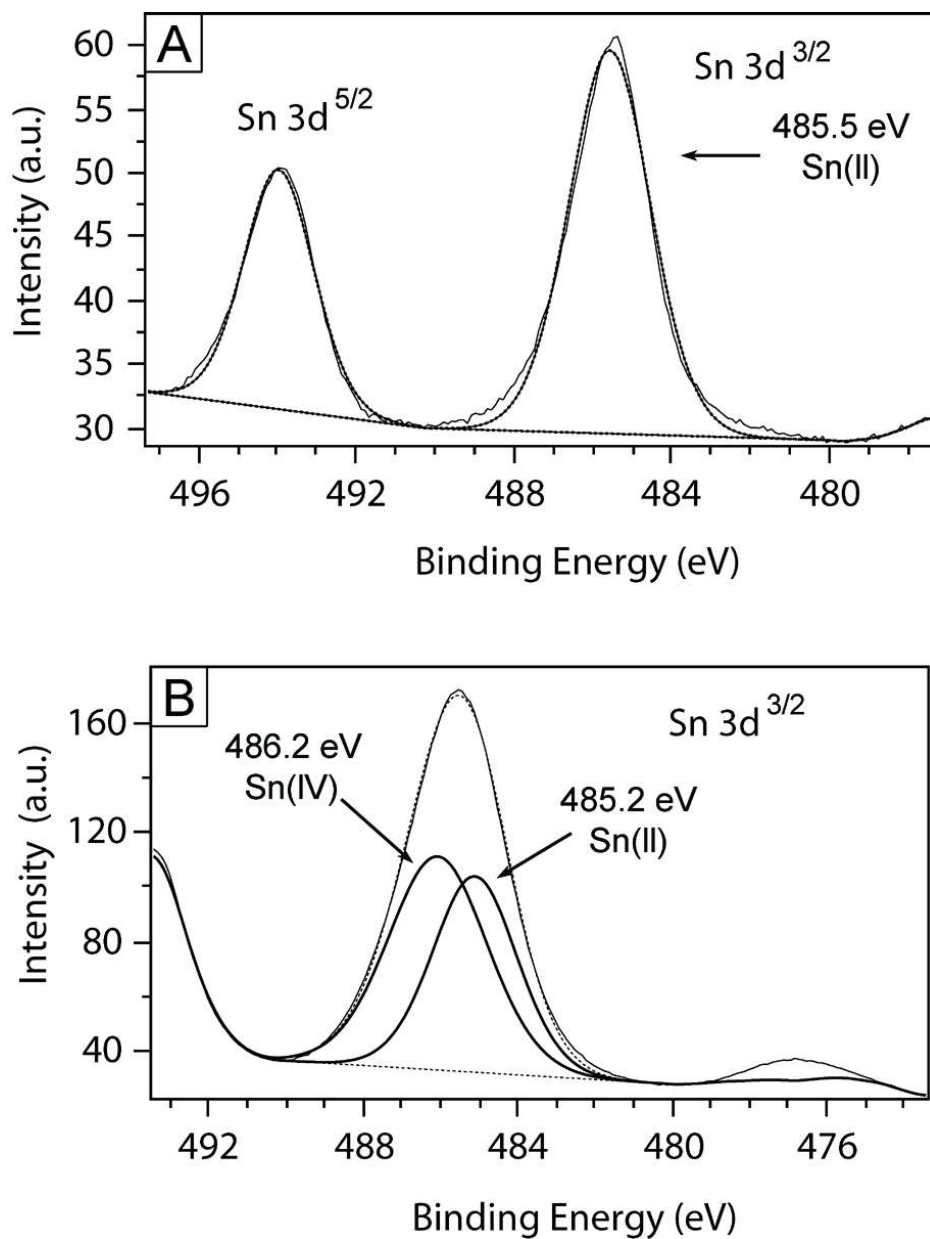


Figure S4. XPS data for (A) precursor nanowires and (B) partially converted nanowires (calcined at 500 °C for 30 min). The peak positions in both figures had been calibrated with the adventitious carbon at 284.5 eV. In (A), the Sn 3d^{3/2} peak centered at 485.5 eV indicated a 2+ oxidation state for the Sn in precursor nanowires. In (B), the appearance of a peak at higher binding energy (486.2 eV) indicates the formation of a new Sn(IV) oxidation state (i.e., SnO₂) for the partially calcinated sample. The peak at 485.2 eV can be attributed to the un-oxidized Sn(II) species in this sample.

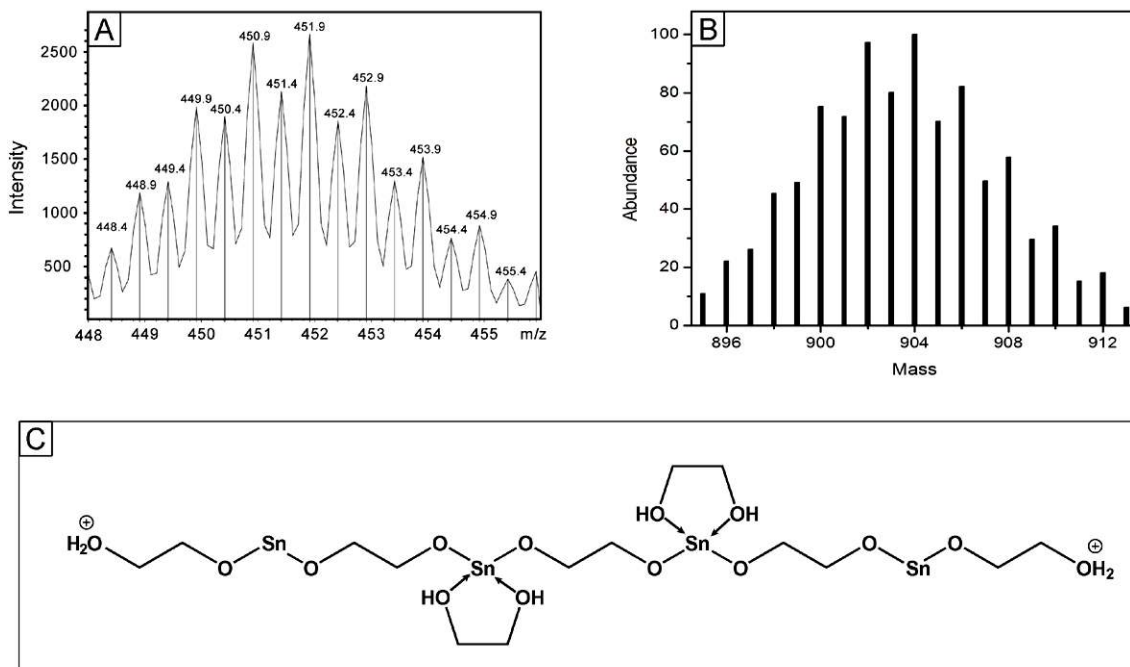


Figure S5. (A) A mass spectrum of the sample taken from the supernatant solution of the reaction mixture, and the pattern could be identified as a Sn_4 oligomeric unit with two charges. (B) The isotopic pattern calculated for such an oligomeric unit. (C) A plausible structure based on the patterns shown in (A) and (B).

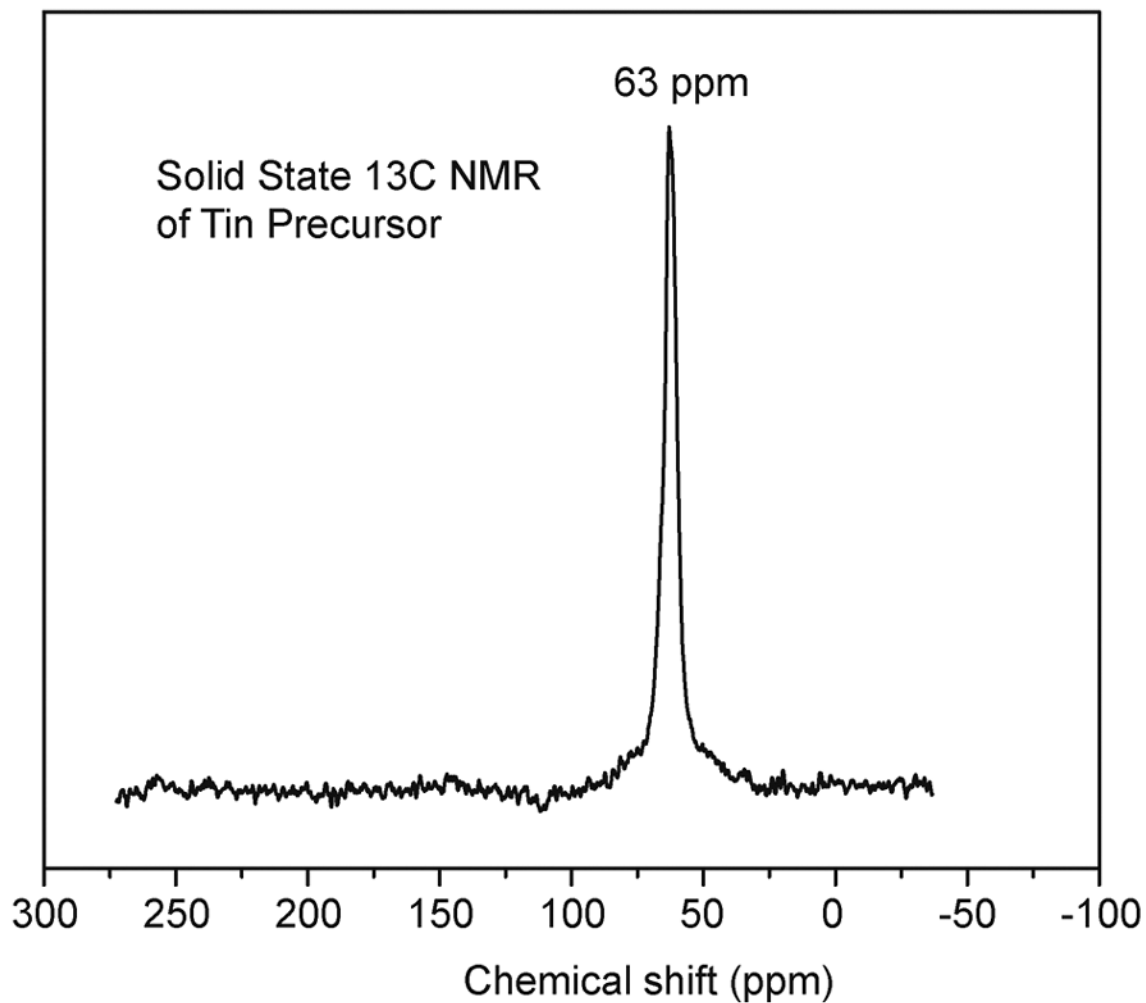


Figure S6. Solid-state ^{13}C NMR spectrum obtained from the precursor nanowires. The peak at 63 ppm can be assigned to the CH_2 units that are directly connected to O atoms (see Fig. 2). The appearance of only one peak suggested that the C atoms in both coordinated and covalently-bonded ethylene glycol units exhibited very similar chemical shifts in the proposed structure.

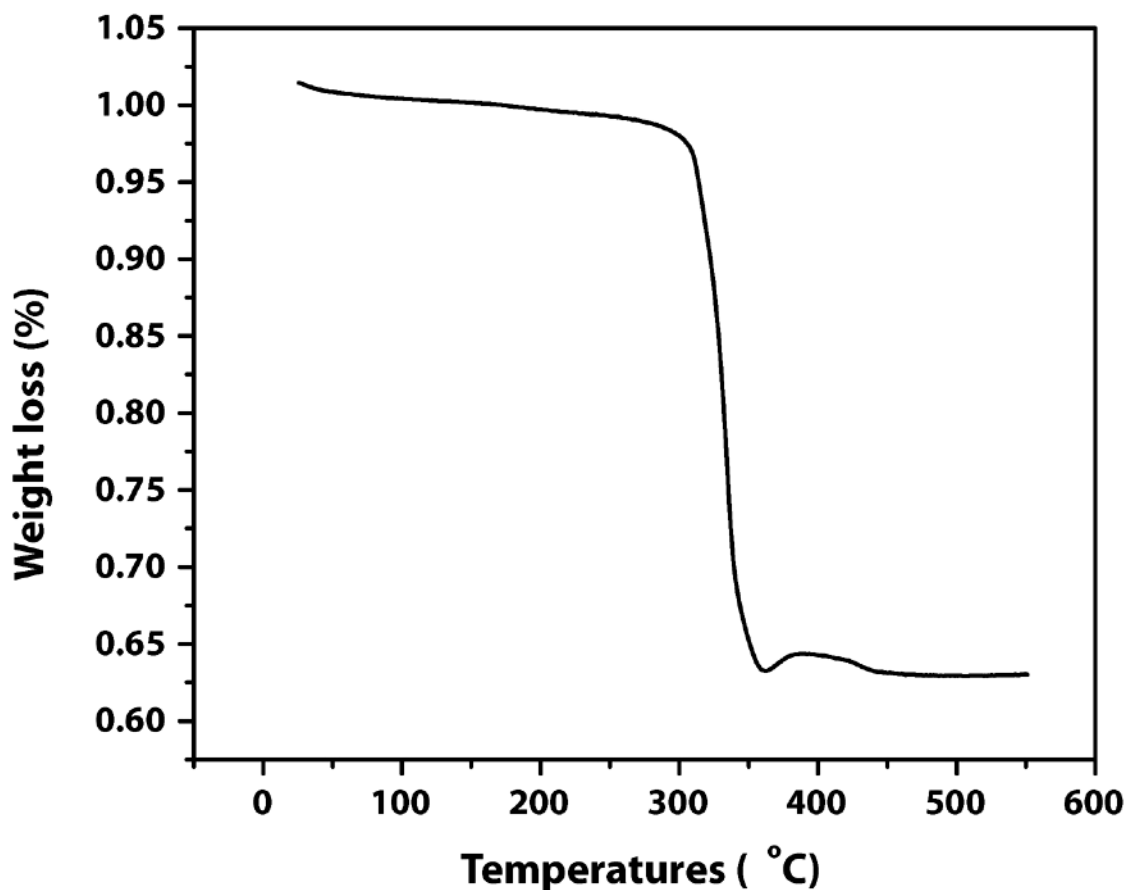


Figure S7. A typical TGA curve obtained for the precursor nanowires under N_2 . Approximately 36% weight loss was observed at a temperature around 325 °C, which corresponds to a calculated value of 37.5% by considering the loss of two coordinated ethylene glycol and four carbon atoms (in the form of ethylene) for each repeating unit.

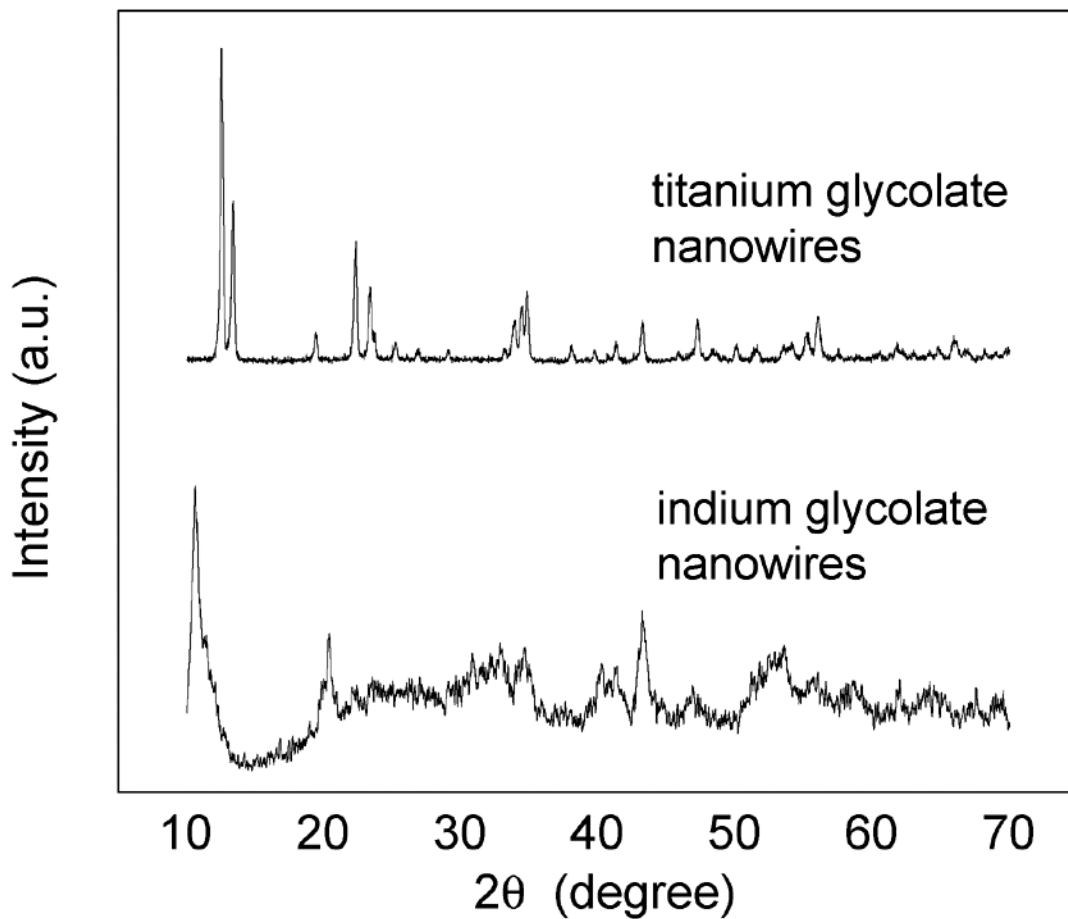


Figure S8. Powder XRD patterns taken from the precursor nanowires to TiO_2 and In_2O_3 before they were calcined. Similar to the XRD pattern for SnO_2 precursor nanowires, diffraction peaks around 10 degrees were also observed for these two precursors.

Experimental procedures for SnO₂ nanowire synthesis:

In a typical procedure, 0.05g SnC₂O₄·2H₂O (partially dissolved in 3 mL EG) and 0.25g PVP (M_w≈55,000) (dissolved in 3 mL EG) were added simultaneously to 5 mL EG that was hosted in a round bottom flask and refluxed at 195 °C under the ambient pressure. During the following 45 min, the cloudy mixture turned into a clear solution. After the solution had been refluxed under constant stirring for 2 h, white precipitates began to appear in the light yellowish solution, indicating the formation of nanowires made of the glycolate precursor. After the reaction had been stopped by cooling down the solution to room temperature, the white precipitates were collected by centrifugation at 4000 rpm, followed by washing with ethanol to remove physically adsorbed PVP and EG. In such a reaction, the tin precursor nanowires could also be synthesized without the use of PVP; however, the quality and the stability of these nanowires would be greatly improved if PVP was present.

Experimental procedures for gas-sensing measurement:

Two gold electrodes (with a separation of 100 μm) were fabricated by first sputtering a thin layer of chromium (~30 nm), followed by another layer of gold (~150 nm) onto a masked glass substrate. The precursor nanowires were cast as a thin film (~5×5×0.5 mm³) spanning across the two gold electrodes by using a mixture of the as-synthesized white precipitate and ethanol. After calcination in air at 500 °C for 1 h, silver paste and copper wires were used to connect the leads of gold electrodes to the instrument. All results shown in Fig. 3 were obtained from the same sensor, which was hosted in a closed plastic tube (~50 mL in size) equipped with appropriate inlets and outlets for gas flow. The two copper wires coming out of the host tube were connected to a Keithley 236 sourcemeter, which served as both voltage source and current reader. Each pristine sensor (in air) was found to exhibit the typical behavior of a varistor, showing an exponential decay in resistance as the voltage was ramped up. For consistency, a potential of 10 V was applied across the two gold electrodes for all measurements, and the air coming from an ordinary fume hood was used as the background gas. Under these conditions, the resistance for a typical sensor was in the range of 5 to 10 gigaohms.