

## Supplementary information

### **Self-activated ultrahigh chemosensitivity of oxide thin film nanostructures for transparent sensors**

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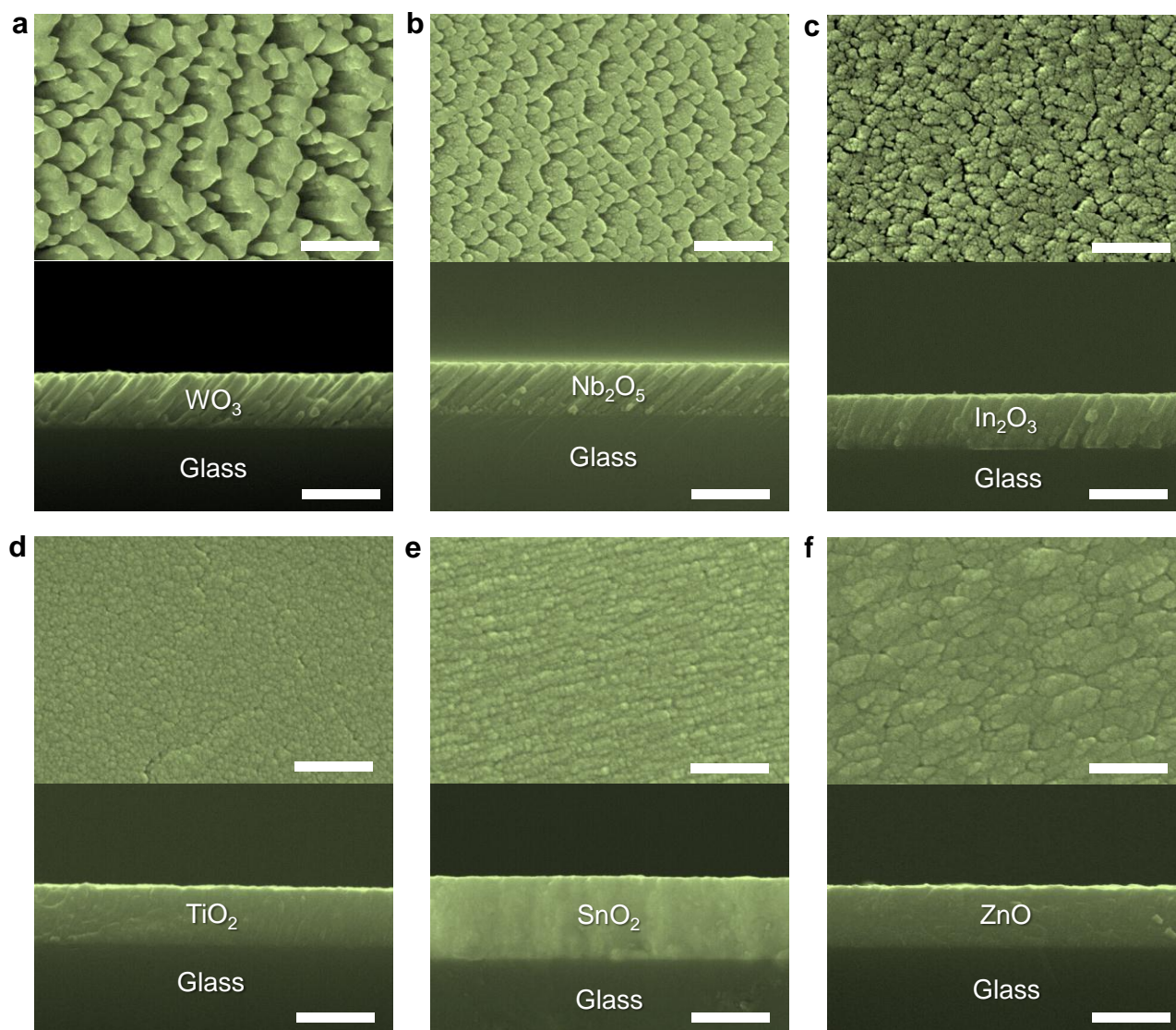
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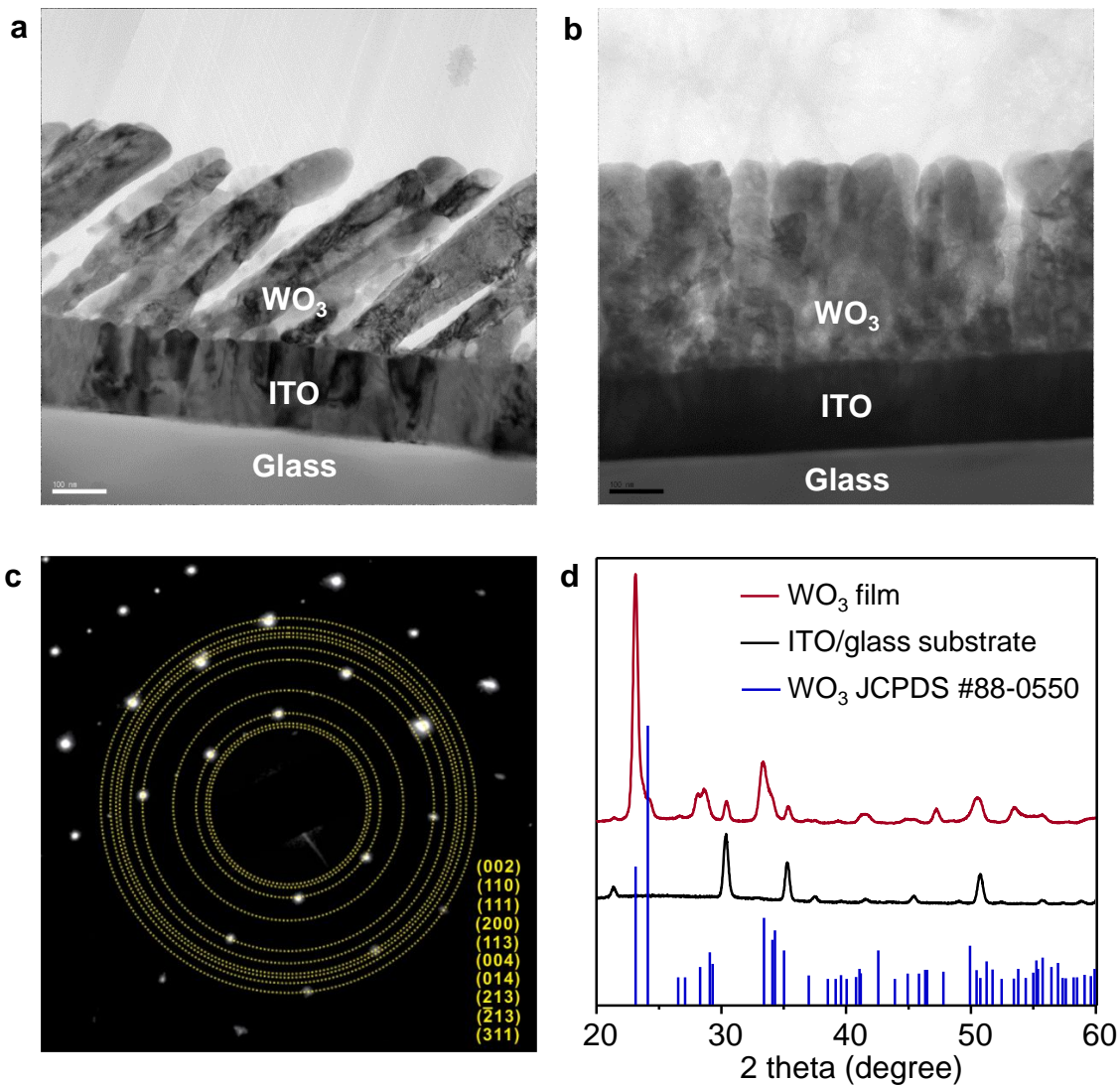
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**Supplementary Table S1.** Ambient air quality standard (AAQS) levels of European Union (EU), United States (US) and Korea for CO, NO<sub>2</sub>, SO<sub>2</sub> pollutants which are considered harmful to public health and the environment. More detailed information about the AAQS levels is available on <http://www.airkorea.or.kr> and <http://www.epa.gov/air/airpollutants.html>.

Pollutant	Averaging time	Level		
		EU	US	Korea
NO <sub>2</sub>	1 year	21 ppb	53 ppb	30 ppb
SO <sub>2</sub>	1 hours	130 ppb	75 ppb	150 ppb
CO	8 hours	8.6 ppm	9 ppm	8.6 ppm

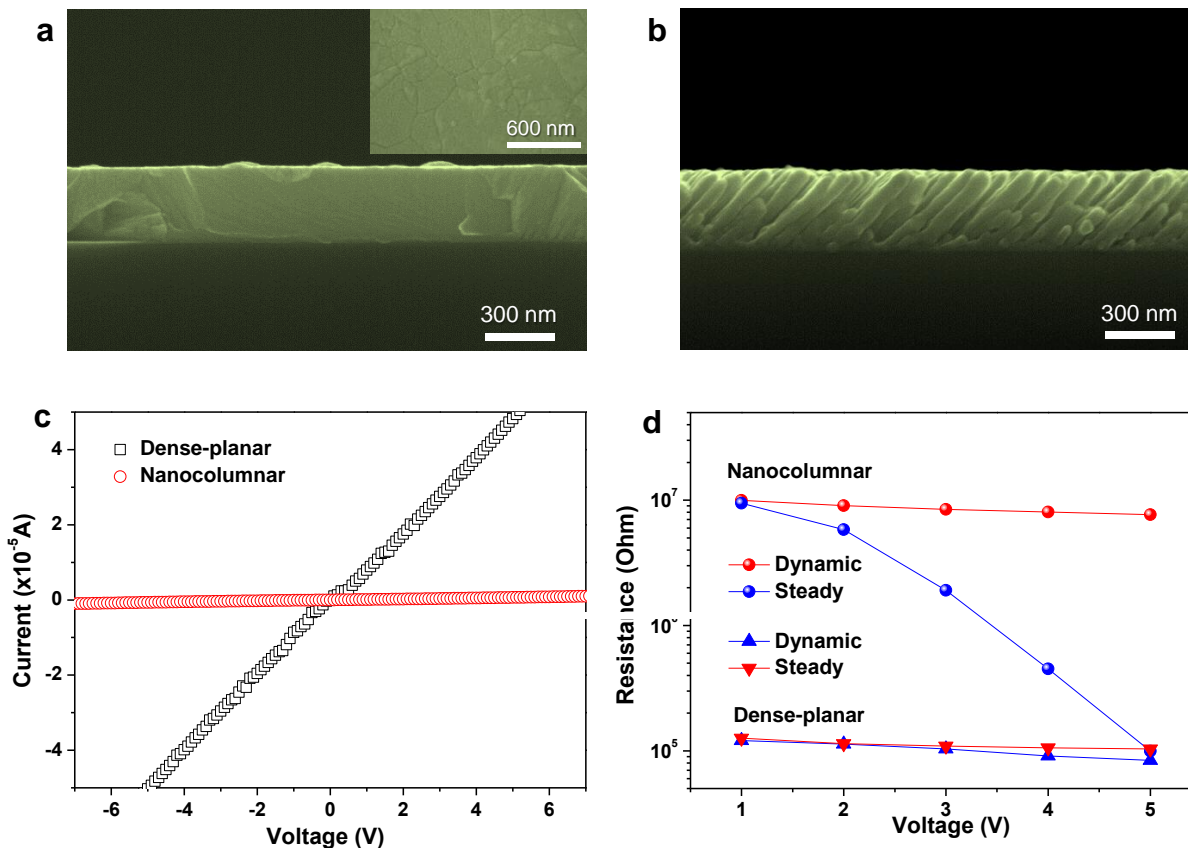


**Supplementary Figure S1 | Various metal oxide thin films by GAD. a–f,** Cross-sectional and plain-view and cross-sectional SEM images of  $\text{WO}_3$  (a),  $\text{Nb}_2\text{O}_5$  (b),  $\text{In}_2\text{O}_3$  (c),  $\text{TiO}_2$  (d),  $\text{SnO}_2$  (e), and  $\text{ZnO}$  (f) thin films. Scale bar, 600 nm.

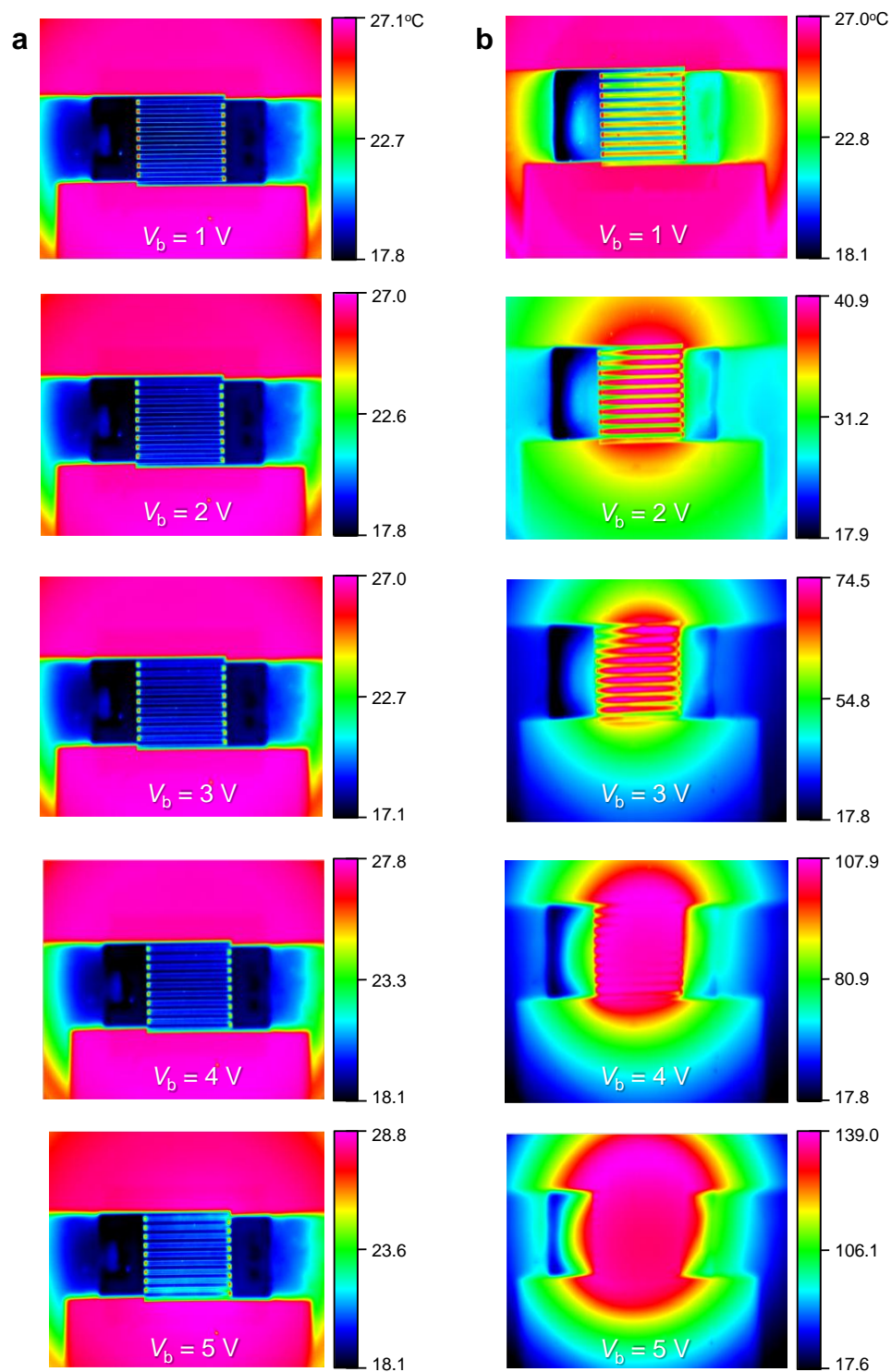


**Supplementary Figure S2 | Structural characterizations of nanocolumnar WO<sub>3</sub> films.**

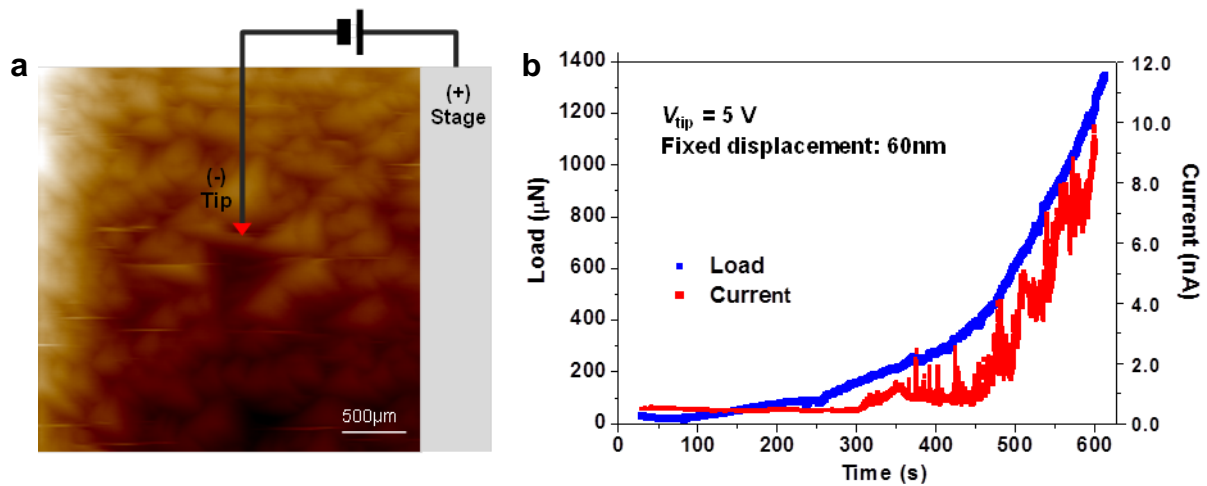
**a,b**, Cross-sectional TEM images of nanocolumnar WO<sub>3</sub> film on ITO electrodes cut along **(a)** and cross **(b)** the ITO IDEs. Scale bar, 100 nm. **c**, Selected area diffraction pattern from TEM for the nanocolumnar WO<sub>3</sub> film. The dot-lined circles corresponds to *d*-spacings of the monoclinic WO<sub>3</sub> phase with lattice parameters of  $a = 5.261 \text{ \AA}$ ,  $b = 5.128 \text{ \AA}$ ,  $c = 7.650 \text{ \AA}$  and  $\beta = 92.050^\circ$ . **d**, Glancing angle X-ray diffraction patterns of a bare ITO/glass substrate and of a nanocolumnar WO<sub>3</sub> film on the substrate. The reflections of the monoclinic phase of WO<sub>3</sub> (JCPDS # 88-0550) are presented with blue lines.



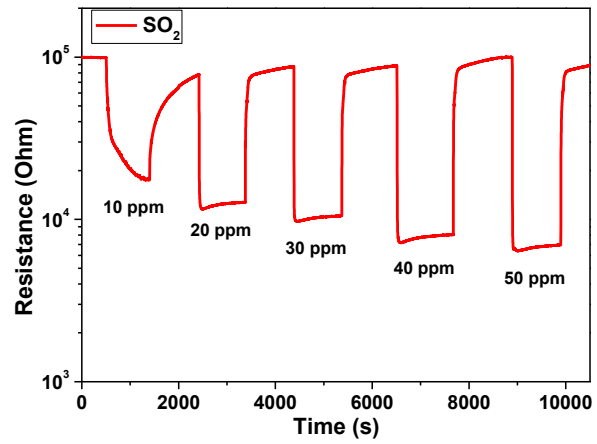
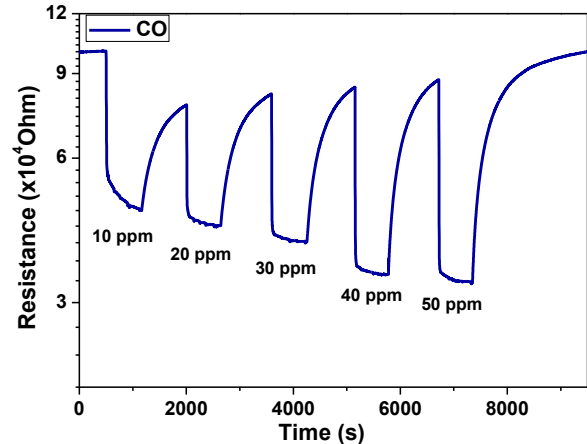
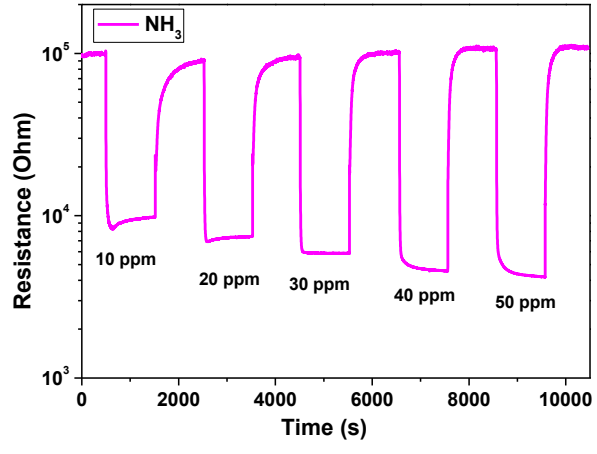
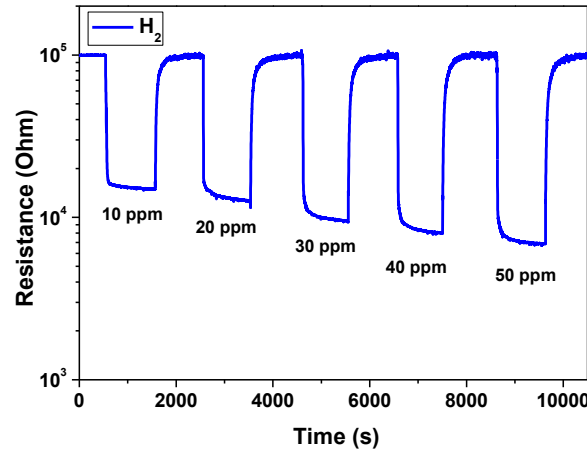
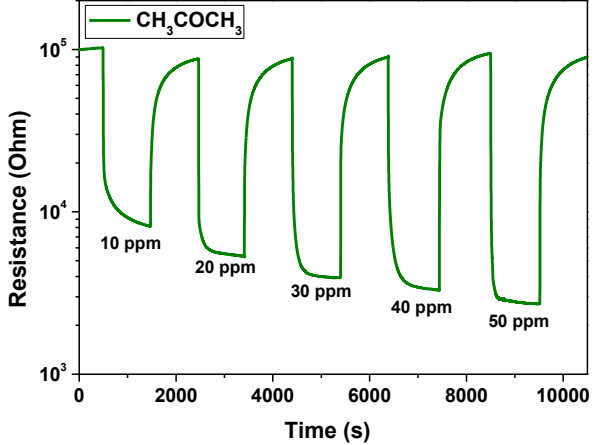
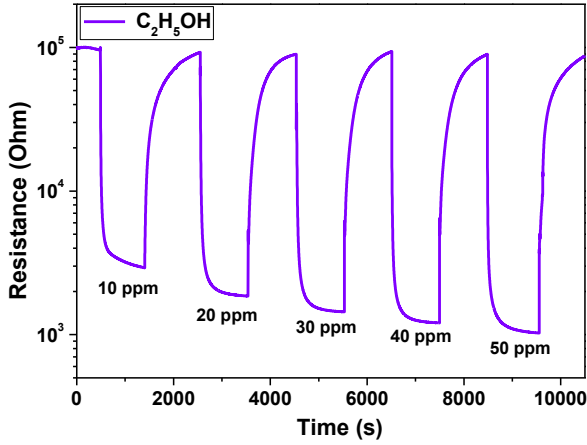
**Supplementary Figure S3 | Morphological and electrical properties of dense-planar and nanocolumnar  $\text{WO}_3$  thin film sensors.** **a,b** Cross-sectional SEM image of the  $\text{WO}_3$  sensing films of the plain  $\text{WO}_3$  thin film sensor (**a**) and the nanocolumnar  $\text{WO}_3$  thin film sensor (**b**). Insets: Plain-view SEM images. **c**, Current-voltage ( $I$ - $V$ ) characteristics of the dense-planar and nanocolumnar  $\text{WO}_3$  thin film sensors. **d**, Resistances of the sensors as a function of the applied bias voltage. Dynamic resistances were evaluated from the  $I$ - $V$  curves in **c**. Steady resistances were measured 10 min later after applying the bias voltage. The large difference between dynamic and steady resistances for the nanocolumnar sensor indicates self-heating in the sensing film.



**Supplementary Figure S4 | Self-activation in sensors. a,b,** Thermographic images of the plain  $WO_3$  thin film sensor (a) and the nanocolumnar  $WO_3$  thin film sensor (b) as a function of the applied bias voltage ( $V_b$ ).

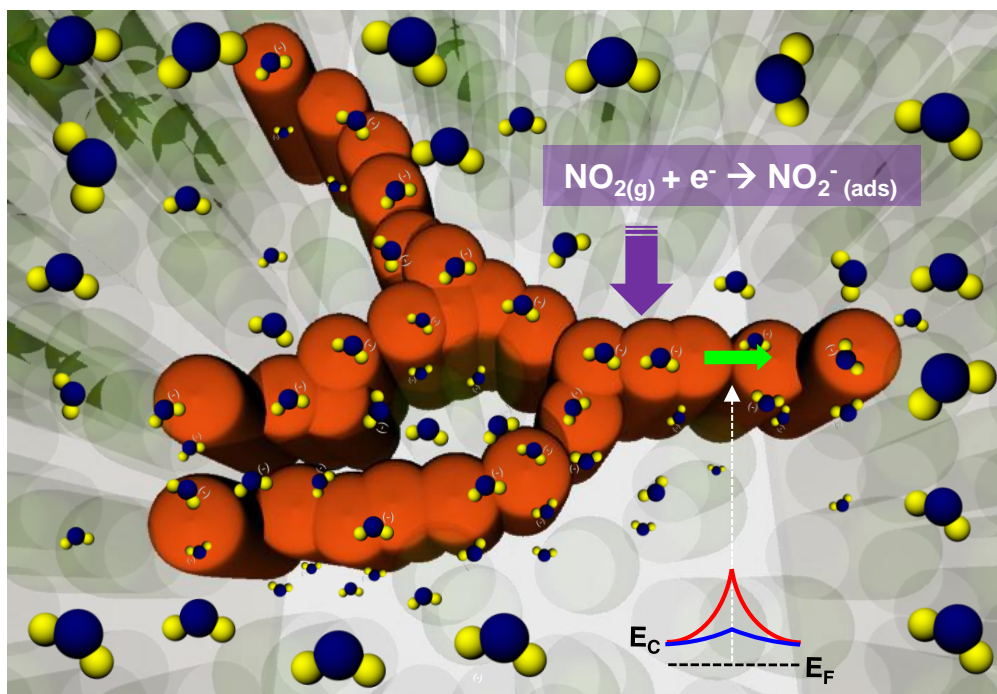


**Supplementary Figure S5 | Nano ECR measurements of the nanocolumnar  $\text{WO}_3$  thin film sensor.** **a**, SPM(Scanning Probe Microscope) image showing location of measurement on the clustered nanocolumns. **b**, Force and current as a function of time at a fixed displacement of 60nm. The increase of force and current with time at the tip implies the thermal expansion of the nanocolumnar film due to joule heating.

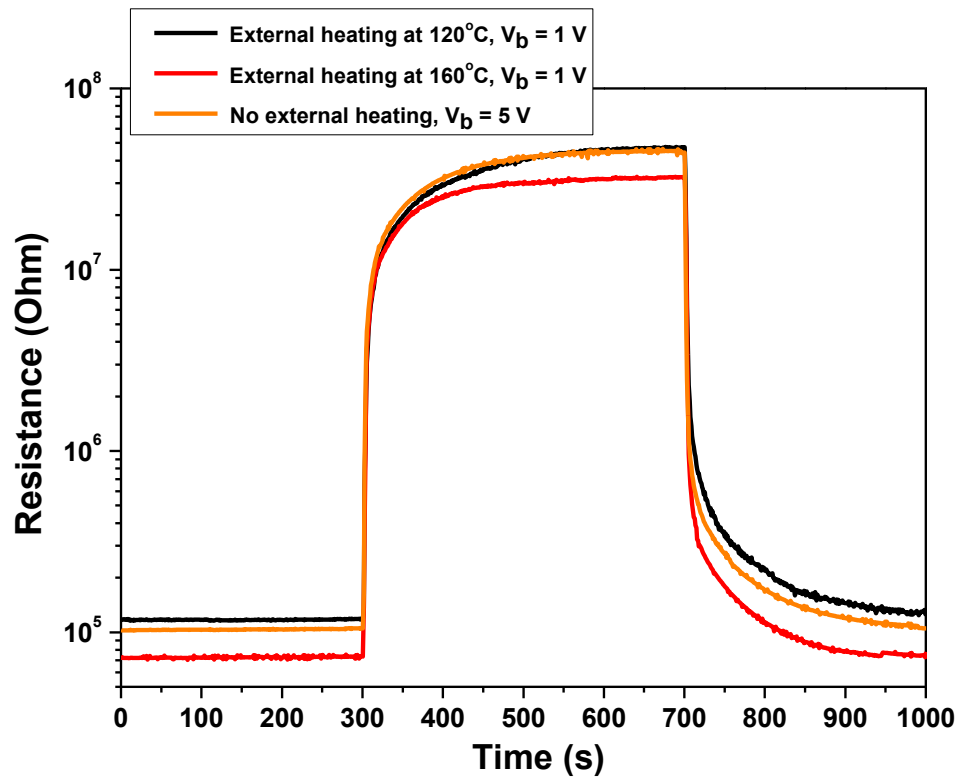


**Supplementary Figure S6 | Responses of the nanocolumnar WO<sub>3</sub> thin film sensor to various gases. The measurements were carried out without external heating at the applied bias voltage of 5 V. Sensor shows linear change in response with varying concentration of test gas,.**

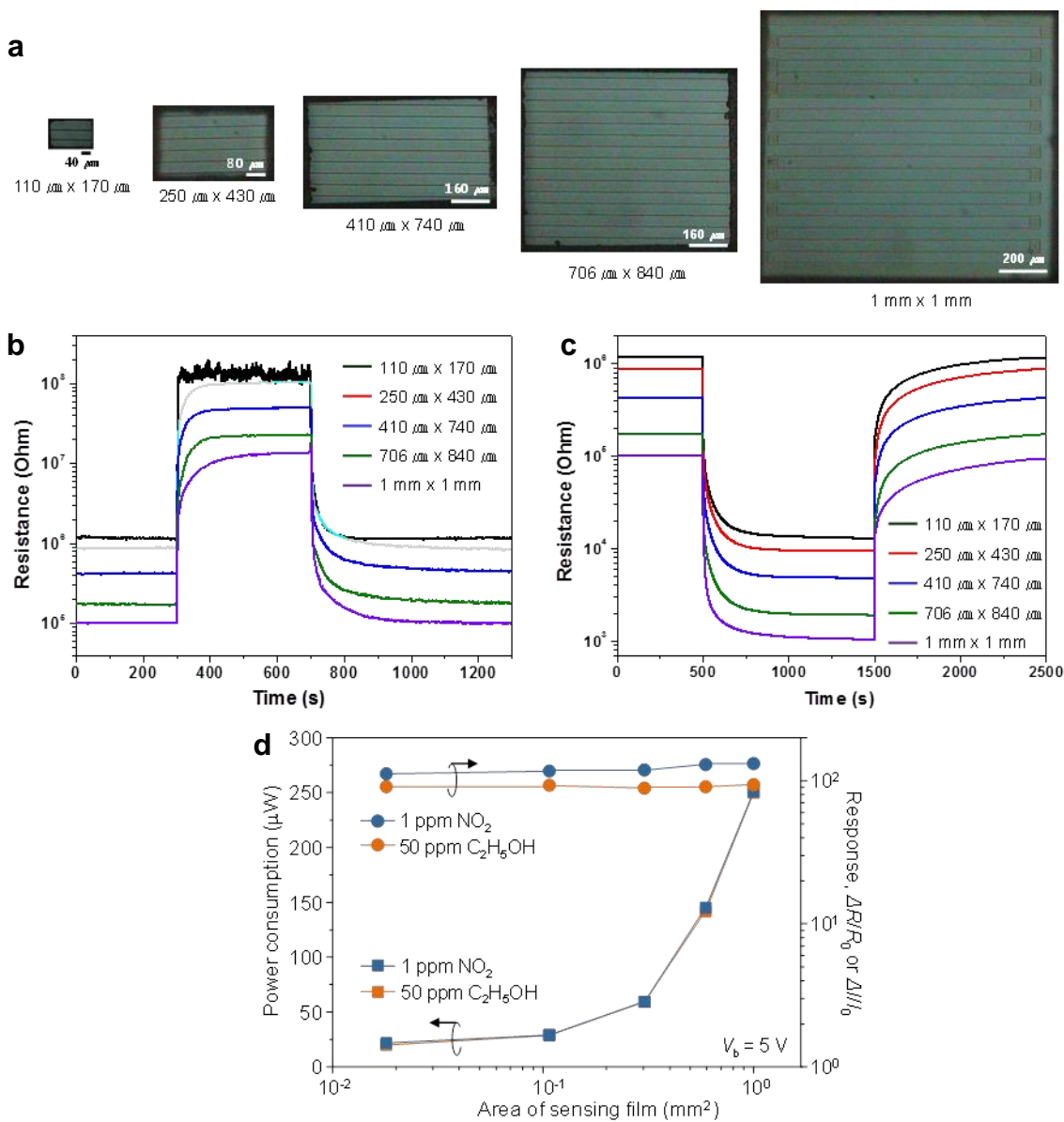




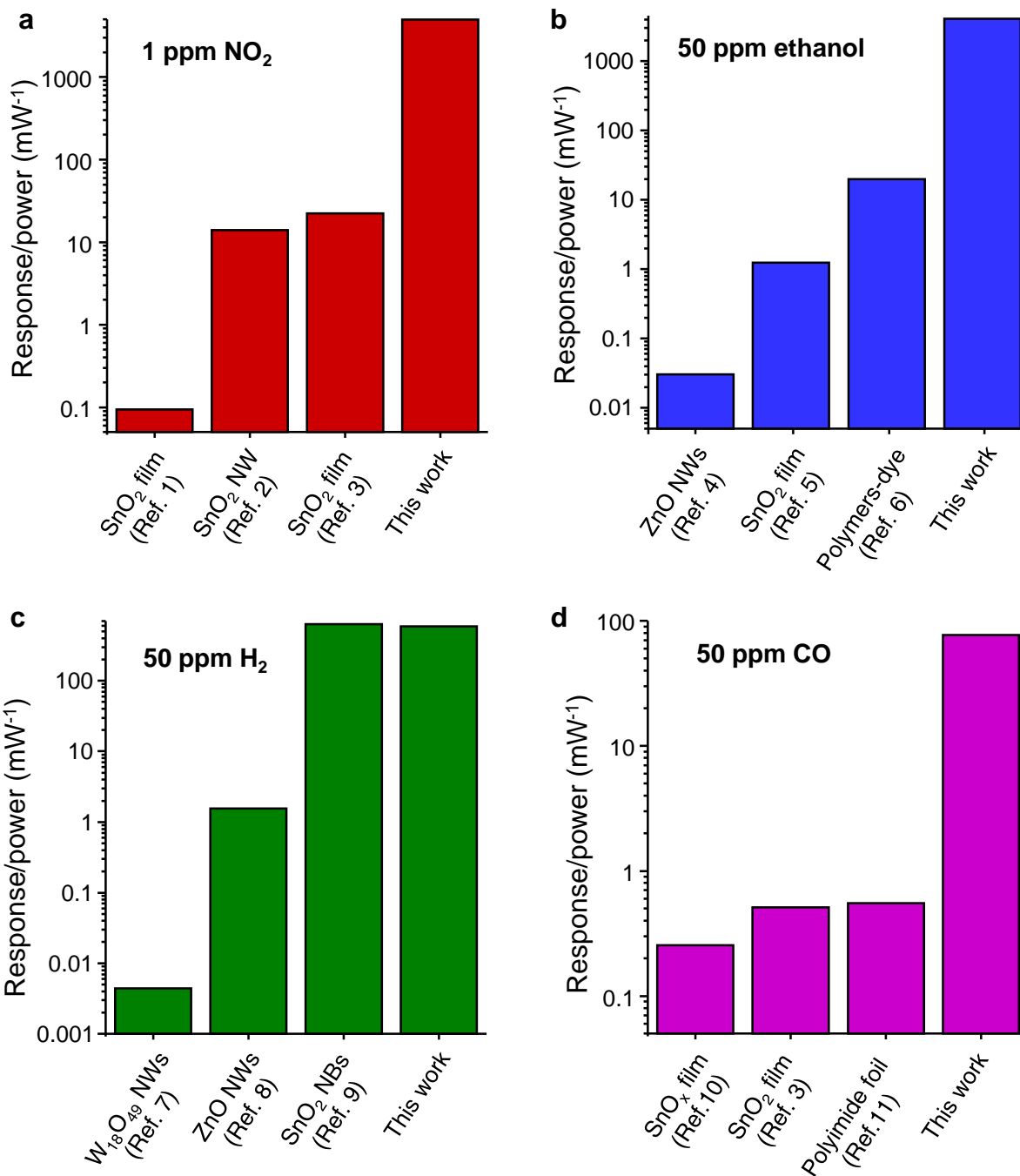
**Supplementary Figure S7** | Schematic illustration of the  $\text{NO}_2$  sensing mechanism of the nanocolumnar  $\text{WO}_3$  thin film sensor. The gas molecules easily access the active nanocolumns, which act as current pathways, and remains hot due to self-heating. At the narrow neck, a high potential barrier for current flow is formed. The green arrow indicates current flow. The lower conduction band edges (blue lines) correspond to the potential barrier in air and the upper conduction band edges (red lines) correspond to the barrier that arises from exposure to  $\text{NO}_2$ .



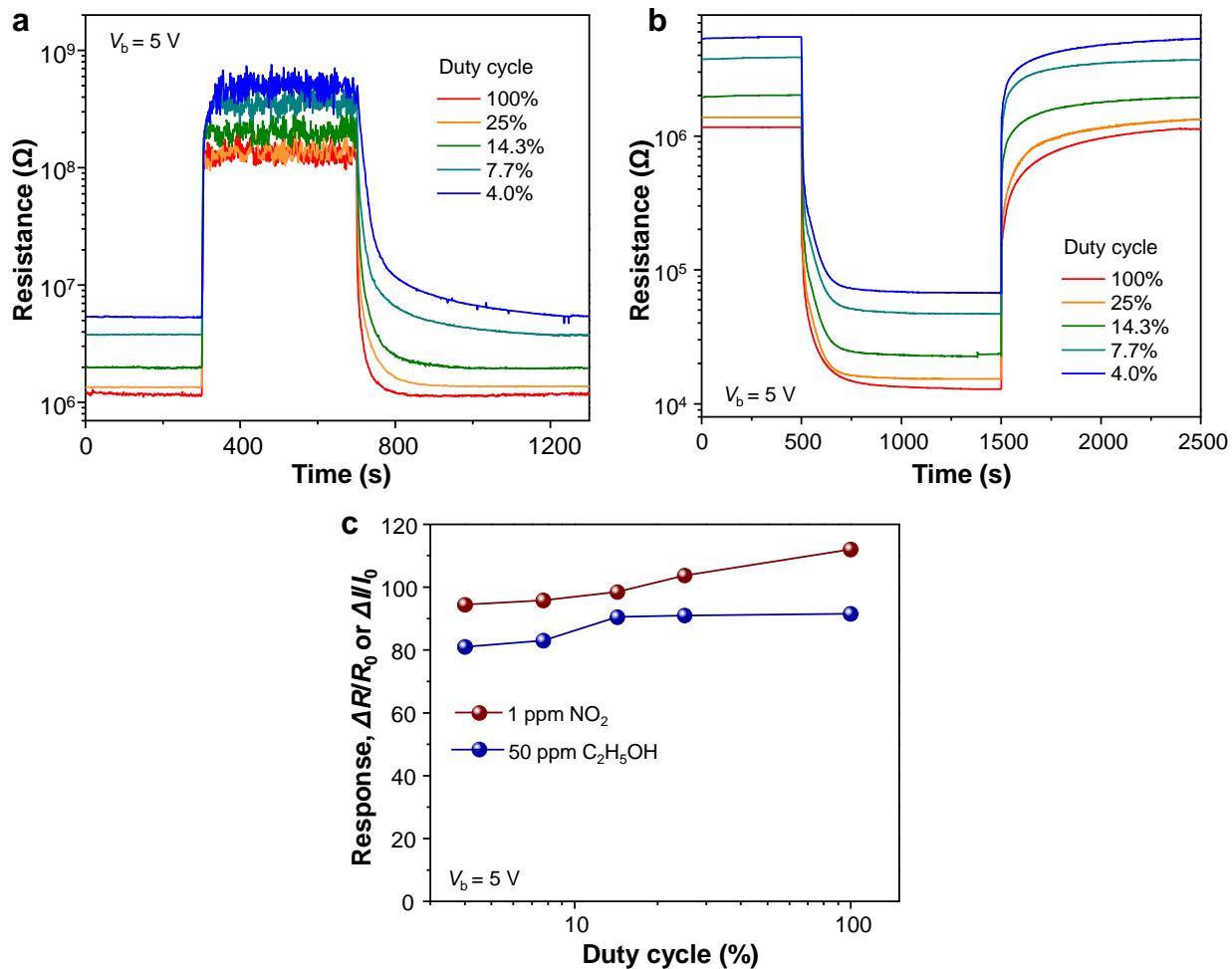
**Supplementary Figure S8** | Comparison of the response of the nanocolumnar  $\text{WO}_3$  thin film sensor to 5 ppm  $\text{NO}_2$  with and without external heating. For measurements with external heating, an applied bias voltage of 1 V was used to minimize self-heating in the film.



**Supplementary Figure S9 | Dependence of sensor response and power consumption on the area of the sensing film.** **a**, Optical microscopy images of 5 different areas of nanocolumnar  $\text{WO}_3$  thin film sensors. **b,c**, Sensing transients of the nanocolumnar  $\text{WO}_3$  thin film sensors with different sensing area to 1 ppm  $\text{NO}_2$  (**b**) and 50 ppm ethanol (**c**). The applied bias voltage to the sensors was 5 V. **d**, Power consumption and response of nanocolumnar  $\text{WO}_3$  thin film sensors to 1 ppm  $\text{NO}_2$  and 50 ppm  $\text{C}_2\text{H}_5\text{OH}$  as a function of the area of the sensing film.



**Supplementary Figure S10 | Comparison of figure of merit for our sensor with state-of-art chemoresistive sensors. a–d,** Response/power values of previously reported high performance chemoresistive sensors<sup>1–11</sup> and our sensor to 1 ppm NO<sub>2</sub> (a), 50 ppm ethanol, 50 ppm H<sub>2</sub>, and 50 ppm CO.



**Supplementary Figure S11 | Dependence of sensor response and power consumption on the duty cycle of pulsed bias voltage. a,b,** Sensing transients of a nanocolumnar  $\text{WO}_3$  thin film sensor with  $100\ \mu\text{m} \times 170\ \mu\text{m}$  sensing area to 1 ppm  $\text{NO}_2$  (a) and 50 ppm ethanol (b). The applied bias voltage to the sensors was 5 V. **c,** Response of the nanocolumnar  $\text{WO}_3$  thin film sensor to 1 ppm  $\text{NO}_2$  and 50 ppm  $\text{C}_2\text{H}_5\text{OH}$  as a function of sensing area.

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