Electronic Supplementary Information For

Morphological and crystal structural control of tungsten trioxide for highly sensitive NO_2 gas sensors

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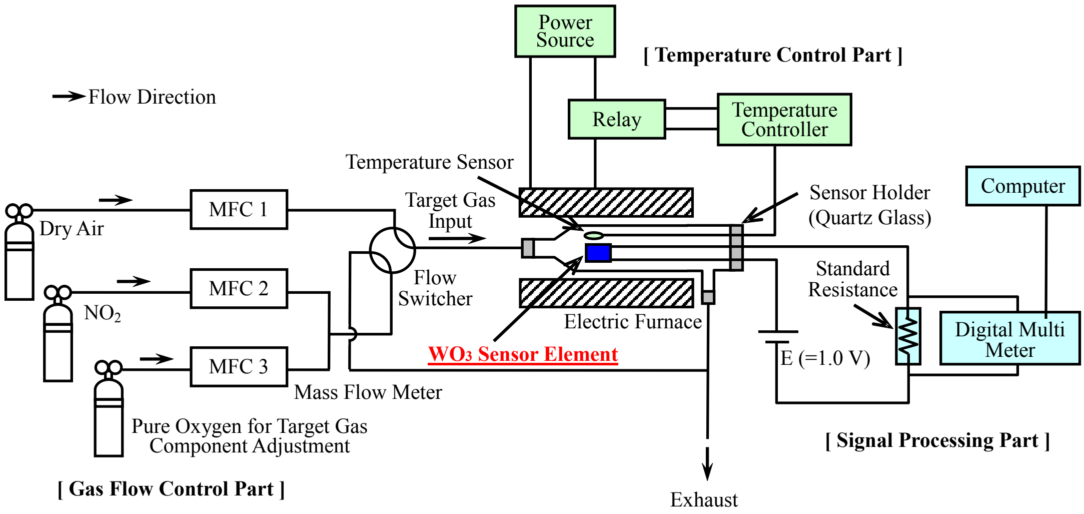

Fig. S1. Schematic diagram for sensing measurement equipment to dilute NO_2.

Sensing Measurement Method

When “Dry Air” was selected as “Target Gas” by using “Flow Switcher”, “Dry Air” was introduced into “Electric Furnace”. The flow rate of “Dry Air” was adjusted to 100 sccm (standard cubic centimeter per minute) by a mass flow controller 1 (MFC1). The operating temperature of “Electric Furnace” was set to be a predetermined temperature such as 200 °C, which was fixed by a Proportional-Integral-Derivative Controller (PID Controller): “Temperature Controller”. The voltage of “Standard Resistance (Rs)” connected directly to “WO_3 Sensor Element”, was monitored as an output voltage by “Digital Multi Meter” after the temperature reached the set-value of PID. When the initial output voltage was stabilized at the operating temperature under a stream of “Dry Air”, “Target Gas” was changed from “Dry Air” to “NO_2”, by using “Flow Switcher”. After exposed to “NO_2” for 3 min, “Target Gas” was changed from “NO_2” to “Dry Air”. The output voltage was continuously monitored until reached the initial voltage in “Dry Air”.

Resistance in air (Ra) and Resistance in NO_2 (Rg) were calculated by the following equation.

$$R = [(E/V)-1]\ Rs$$

where “R” is the resistance of “WO_3 Sensor Element” and “E” is the supplied voltage.

Actually, “NO_2” is composed of 5.01-ppm NO_2 diluted with N_2. When NO_2

concentration was adjusted to be 0.5-ppm by MFC3, the flow rate of MFC3 was set to 20.0 sccm. In this case, the flow rate of "Dry Air" was set to 87.5 sccm, and that of "O_2" to 2.5 sccm by MFC2. The addition of "O_2" by MFC2 means adjusting the O_2 concentration to the same value of 21% as the atmospheric O_2 concentration.

NO_2 concentration of NO_2-containing N_2, α (ppm), and NO_2 concentration predetermined, β (ppm), are calculated using the flow rate of "Dry Air", X (sccm), that of "O_2", Y (sccm), and that of "NO_2", Z (sccm), as follows.

$$Z = (\beta/\alpha) \times 100$$

$$Y = (Z/0.79) \times 0.21 \approx 25 \times (\beta/\alpha)$$

$$X = 100 - Y - Z = 25 \times [4 - 5 \times (\beta/\alpha)]$$

Table S1. Ratio of W^{6+} and W^{5+}, that of surface O^{2-}, OH^-, and H_2O, and binding energies of $W4f_{5/2}$, $W4f_{7/2}$, and O1s peaks for as-prepared C-m-WO_3 and H-h-WO_3.

Sample	W4f		Sample	O1s		
	W^{6+} [%]	W^{5+} [%]		O^{2-} [%]	OH^- [%]	H_2O [%]
C-m-WO_3	98.3	1.7	C-m-WO_3	80.4	4.9	14.7
H-h-WO_3	99.3	0.7	H-h-WO_3	60.0	38.1	1.9
C-m-WO_3	Binding energies (eV)		C-m-WO_3	Binding energies (eV)		
$W4f_{5/2}$ peaks	35.9	-	O1s peaks	530.7	532.4	533.4
$W4f_{7/2}$ peaks	38.0	36.9				
H-h-WO_3	Binding energies (eV)		H-h-WO_3	Binding energies (eV)		
$W4f_{5/2}$ peaks	36.1	-	O1s peaks	530.8	531.6	532.1
$W4f_{7/2}$ peaks	38.2	37.0				