

Supporting Information for

Unique Pd/PdO-In₂O₃ heterostructures for the highly efficient detection of triethylamine

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Experimental Section

All chemicals are of analytical grade and were used without any further purification.

Synthesis of In(OH)₃: A simple solvothermal method was used to synthesize In(OH)₃ nanocubes. In a typical experiment, 0.3 g of In(NO₃)₃·XH₂O and 0.15 g of urea were dissolved in 40 ml of deionized water with thorough stirring to dissolve for 20 min, then the solution was put into 150 ml of polytetrafluoroethylene lining, and then the reaction kettle was placed in an electric heating blast drying oven and heated to 160°C and kept for 4 h, and then the reaction kettle was naturally cooled to room temperature and collected

samples. The samples were washed several times with deionized water and anhydrous ethanol and then dried in a drying oven at 50°C to obtain white $\text{In}(\text{OH})_3$ powder.

Synthesis of Pd-In₂O₃: Take a certain amount of $\text{In}(\text{OH})_3$ into a muffle furnace, and anneal at 350°C for 2 h (the heating rate is 5°C/min) to obtain yellow In_2O_3 powder. Take 0.05 g of In_2O_3 powder, put it into a beaker, add 10 ml of anhydrous ethanol, then ultrasonically treat it for 10 min, and then continuously stir on a magnetic heating stirrer, add a certain amount of 1 mol/L $\text{Pd}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ (According to the mass ratio of In_2O_3 , 0.8%Pd- In_2O_3 needs $\text{Pd}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ solution 1.736 μL , 1.5%Pd-3.255 μL , 2%Pd-4.34 μL , similarly.), after stirring for a while, add a 1 mol/L NaBH_4 solution equal to the $\text{Pd}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ solution to the mixture, and then keep stirring, after all the anhydrous ethanol is volatilized, get Pd-In₂O₃.

Synthesis of Pd/PdO-In₂O₃: Take 0.05 g of $\text{In}(\text{OH})_3$ powder and put it in a beaker, then add 10 ml of anhydrous ethanol to the beaker, after that, the mixture was sonicated for 10 min to disperse the $\text{In}(\text{OH})_3$ uniformly, then a certain amount of 1 mol/L $\text{Pd}(\text{NO}_3)_3 \cdot \text{XH}_2\text{O}$ solution was added to the mixture (According to the mass ratio of $\text{In}(\text{OH})_3$, 0.8%Pd- $\text{In}(\text{OH})_3$ needs $\text{Pd}(\text{NO}_3)_3 \cdot \text{XH}_2\text{O}$ solution 1.736 μL , 1.5%Pd-3.255 μL , 2%Pd-4.34 μL , similarly.), and then keep stirring, after all the anhydrous ethanol is volatilized, the gray-black product is collected, after that, the gray-black product was calcined in a muffle furnace at a temperature of 350°C for 2 h (the heating rate was 5°C min⁻¹) to obtain Pd/PdO-In₂O₃.

Characterization

The X-ray powder diffraction (XRD) of the samples was conducted on a D/max-2300 diffractometer (Rigaku Corporation; 35 kV) in a scanning range of 10-90° at a rate of 2°min⁻¹ with Cu K α 1 radiation ($\lambda=1.540\text{\AA}$). The morphology of the samples was recorded by field emission scanning electron microscopy (FESEM, Thermo Fisher Scientific Co. Ltd.). The sample was characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEM-2100 microscope (JEOL Co. Ltd.)

operating at 200 kV. Selected area electron diffraction (SAED) was performed on the above-mentioned transition electron microscopy. The sample was characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) using a ThermoFisher Spectra-300 double corrected transmission electron microscope (Thermo Fisher Scientific Co. Ltd.) operating at 300 kV. The thermal behavior during calcination in the air atmosphere was carried out by thermal gravimetric analysis (TGA/DSC thermogravimetric analyzer, MELER/1600 H). The N₂ adsorption-desorption analysis of the obtained samples was collected on Beth equipment (Bestech Instrument Technology Co. Ltd.) at liquid nitrogen temperature. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Co. Ltd.; S3 1486.6 eV) was investigated on a K-Alpha+ spectrometer with Al K α excitation to observe the chemical binding states of each element. The content of Pd is determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, German Jena Co. Ltd PQ 9000).

Fabrication of gas sensor

The sensor used in the experiment is a thick film type. Pt electrodes are plated on the surface of the rectangular ceramic substrate, and two electrodes are formed on the bottom of the substrate. Through two heating electrodes, the test equipment can adjust the heating power to control the test temperature. The test equipment and gas sensor are shown in Fig. S1. After ventilation and desorption, the corresponding curve of resistance value and time will be obtained. After coordinating and analyzing a large amount of gas sensitivity data, the fitting relationship curve can be analyzed. In this article, the prepared sample is mixed with printing oil with a mass ratio of 1:1 and ground uniformly. The paste is then printed on the circular area on the top of the sensor by screen printing technology. Finally, the prepared sensor is annealed in a muffle furnace for 2 h. Install the cooling device carefully on the SD-101 four-channel gas-sensing tester, and then aging in the air at 200°C for 72 h to stabilize the resistance value of the sensor, and then the gas-sensing performance can be measured.

Supplementary Figures

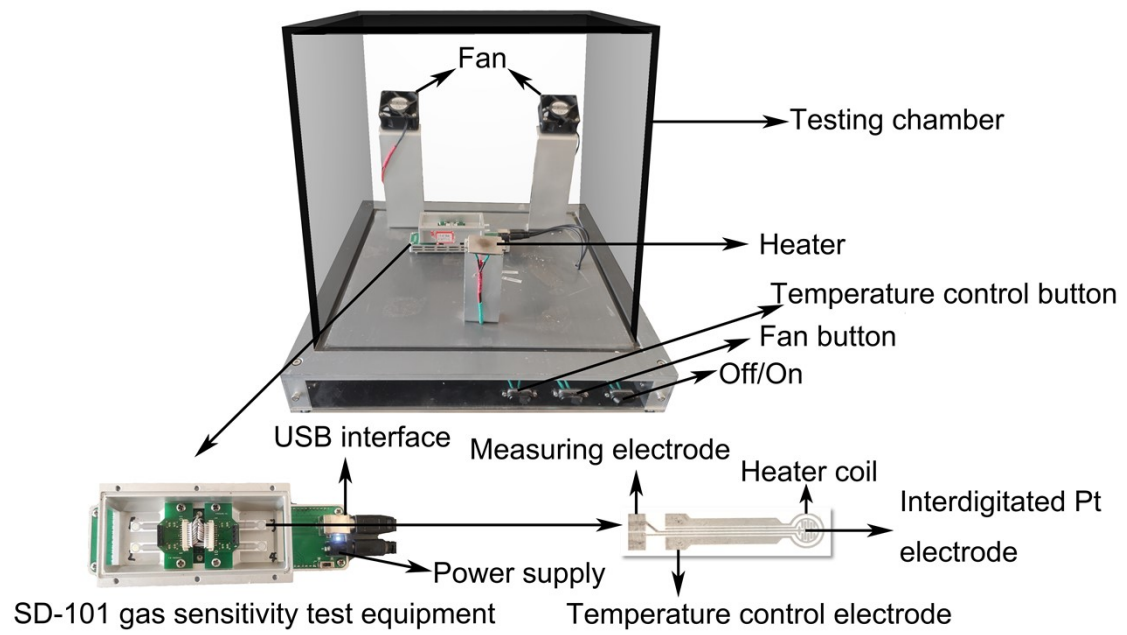


Fig. S1 Gas sensor and gas test platform.

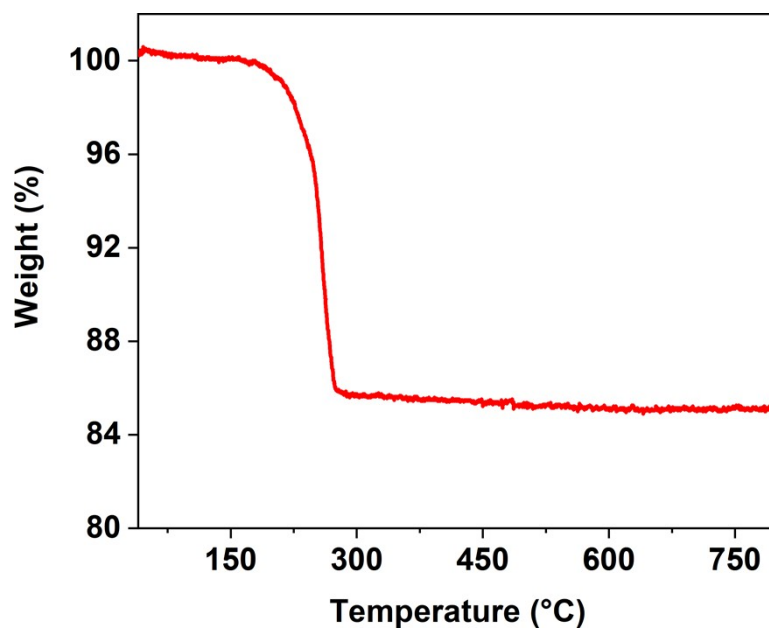


Fig. S2 Thermogravimetric curve of $\text{In}(\text{OH})_3$.

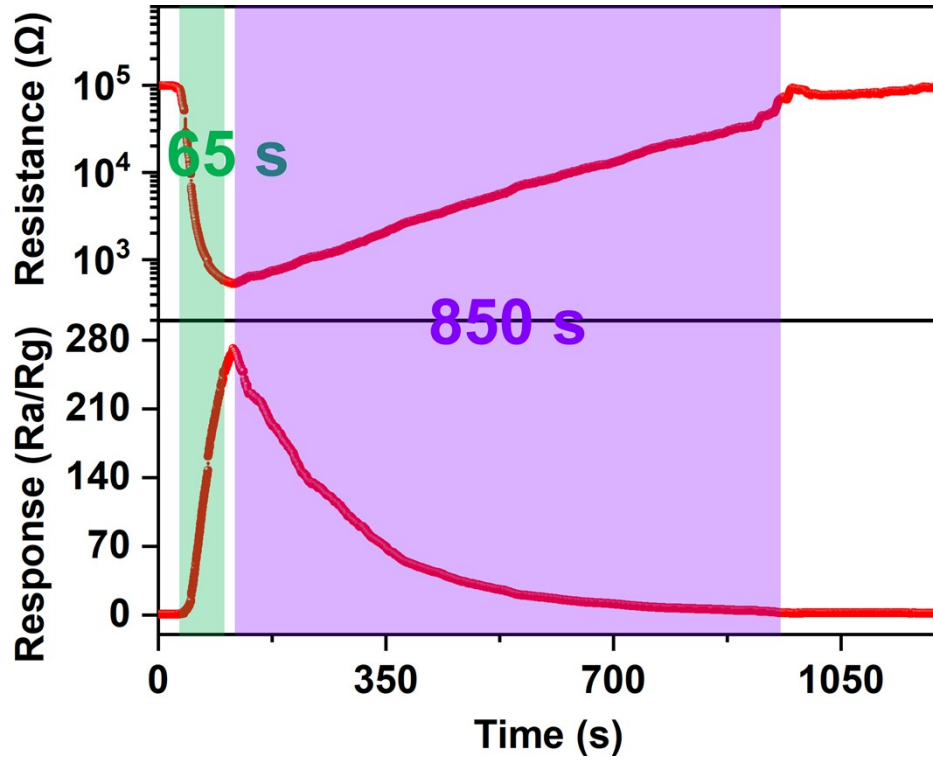


Fig. S3 Transient resistance curve and response-recovery curve of In_2O_3 nanorod sensor to 10 ppm TEA at 150°C .

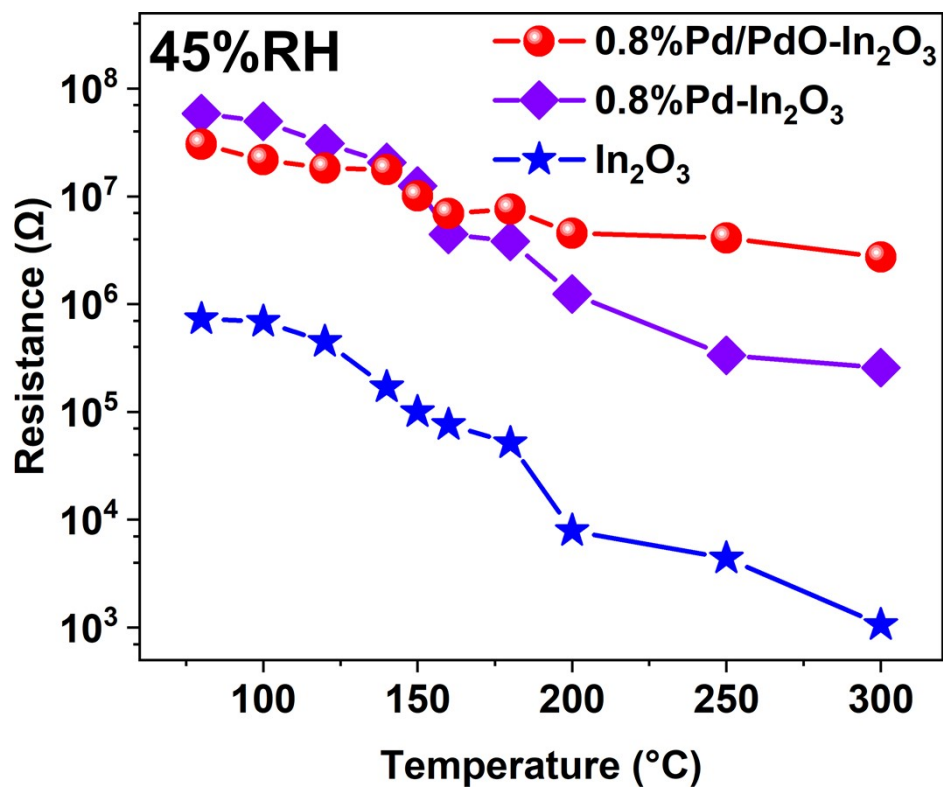


Fig. S4 Resistance of different sensors at different operating temperatures.

Table S1. ICP-OES measurement results of different samples

Sample	0.8%Pd- In ₂ O ₃	0.8%Pd/PdO- In ₂ O ₃	1.5%Pd/PdO-In ₂ O ₃
Pd content (Wt%)	0.68	0.42	1.05

Table S2. Performance comparison between this study and the recently reported triethylamine gas sensor

Material	Concentration (ppm)	Response	T_{res}/T_{rec} (s)	Temperature (°C)	DL (ppm)	Ref
ZnWO ₄ /ZnO	50	108.5	16/12	350	0.15	1
ZnO/BiOBr	100	20.57	4/198	200	0.11	2
YVO ₄ /V ₂ O ₅	100	42.15	4/14	140	NA	3
GaFeO ₃	200	7.4	9/49	200	NA	4
α-Fe ₂ O ₃	50	252.7	2/124	160	0.05	5
Ag-WO ₃	50	5150	189/138	175	<0.1	6
			0			
MoO ₃ /ZnMoO ₄ /CoMoO ₄	10	505.67	36/13	270	0.1	7
SnO ₂ microfiber	100	49.5	14/12	270	2	8
ZnSnO ₃ nanocube	100	57.5	4/1040	350	0.6	9
Au-ZnO	10	276	20/216	200	NA	10
rGO/LaFeO ₃	50	103.5	3/4	240	NA	11
ZnO/Co ₃ O ₄	50	67.8	17/25	240	NA	12
Pd/PdO-In₂O₃ nanorods	10	1380	30/90	150	<0.1	This work

*T_{res}/T_{rec}=Response/Recovery time; DL= Detection limit; Ref=Reference

Reference

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