

Supporting Information

Single-atom silver loaded on tungsten oxide with oxygen vacancies for high performance triethylamine gas sensor

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Experimental synthesis

Preparation of WO₃

The thin films of WO_3 were directly deposited on to the fluorine-doped tin oxide (FTO) substrates by a hydrothermal route (Figure S 1a). In a typical procedure, 0.33 g sodium tungstate dehydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and 0.116 g sodium chloride (NaCl) were dissolved in 50 ml deionized (DI) water with constant magnetic stirring for 10 min. Remarkably, the solution was acidified to a $\text{PH}=1$ by using 3 M HCl to form yellowish white precipitate. Then 0.225 g oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) dissolved in 10 ml DI water, was added drop wise to this precipitate with constant magnetic stirring for 30 min to get a clear transparent solution. The clear transparent solution was transferred to a 100 ml Teflon-lined stainless steel autoclave. A cleaned FTO glass substrate (washed two times with ethanol and three times with DI water) was immersed vertically into the solution. The autoclave was then sealed and maintained at 100 °C for 4 h. After cooling to room temperature naturally, the yellowish film was formed on the surface of the glass substrate, which was centrifugally washed several times with DI water to remove ions and then dried at 60 °C for 24 h in air.

Synthesis of coast-like Ag- WO_3

The synthesis route shows in Figure S 1b. Weigh different AgNO_3 and put it into a 25 ml beaker, mix it into 20 ml ethanol solution (0.005 mol/L, 0.01 mol/L, 0.05 mol/L). Then heat the solution to 50 °C, put FTO glass containing WO_3 film obliquely into the beaker. Grow it at a constant temperature for 5 min, then rinse it with ethanol along the thickness direction of the glass, and dry samples at 60 °C for 6 h. Finally, the dried samples were calcined at 500 °C for 2 h in the air to obtain like coast-Ag/ WO_3 . The

color of the Ag-WO₃ powder was yellow, finally.

Sensor fabrication and sensing test

In the as-prepared of gas sensing materials (pure WO₃, 0.005 M Ag-WO₃, 0.01 M Ag-WO₃, 0.05 M Ag-WO₃), 2 mg gas sensing materials samples were mixed with 2 mg printing oil in mortar, which was ground for 1 min in agate mortar for forming a uniform mash. The mash sensing materials were screen-printed with a mesh on the outer surface of the substrate and dried at 60 °C for 10 min in a drying oven. And then, the devices were sintered at 400 °C for 2 h in an electric furnace to ensure its stability. Finally, the sensing properties were evaluated by HCRK-SD101 gas sensing analyzer (Wuhan HCRK Technology Co. Ltd.) at the relative humidity of 20±10%. The prepared sensors were installed in the test chamber (2.7 L) and then injected with different concentrations of tested gas by a micro syringe. The working temperature can be controlled via adjusting the heating power of the heater coil. The sensors are tested by the static gas sensing system at different temperatures. The response of the gas sensor can be defined as the ratio of the resistance value (R_a) in the fresh air to the resistance value (R_g) in the tested gas. The gas-sensing response (S) for the n-type semiconductor in the measurement was deduced using the following equation:

$$S = R_a/R_g \quad (1)$$

The response and recovery time are defined as the time of the sensor reaching 90 % of the total response change in the process of adsorption and desorption, respectively.

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 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.). Transition Electron Microscopy (TEM) and High resolution Transmission Electron Microscopy (HRTEM) of the size and crystallinity of the grain were performed by a JEM-2100 microscope (JEOL Co. Ltd.) operating at 200 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) were performed on Titan Themis³ G2 300 (Thermo Fisher Scientific Co. Ltd.). X-ray photoelectron spectroscopy (XPS) was investigated on a K-Alpha⁺ spectrometer with Al K excitation (Thermo Fisher Scientific Co. Ltd.; 1486.6 eV) to observe the chemical binding states of each element. The Raman was performed by an inVia Qontor confocal micro Raman spectrometer (RENISHAW apply innovation). The Fourier Transform Infrared spectroscopy (FT-IR) was carried out on FT-IR-2000. UV-vis spectrophotometer (SHIMADZU UV-2600i) was used to analyze the optical properties of the samples, and BaSO₄ was used for baseline correction. Electron paramagnetic resonance (EPR) spectra were recorded in the X band region by a Bruker model E500 spectrometer under the following condition: T=295 K, microwave power 6.325 mW, frequency 9.85 GHz.

Calculation of low limit of detection (LLD) of the sensors.

The sensitivity and the root-mean-square (RMS) deviation at the baseline are used to obtain noise level and the LLD of the sensors. According to the International Union of Pure and Applied Chemistry (IUPAC), as the detection signal is three times higher than the instrument noise level, the theoretical LLD of the sensor can be obtained by correlation calculation. A linear fit of the response to the target gas concentration curve is performed in the linear region, and then the slope (S) is obtained. Then the root-mean-square deviation (RMS) and LLD are calculated using the formulas equation (1) and (2):

$$RMS (ppm^{-1}) = \sqrt{(\sum (X_i - X)^2 / (N - 1))} \quad (1)$$

$$LLD (ppm) = 3RMS/S \quad (2)$$

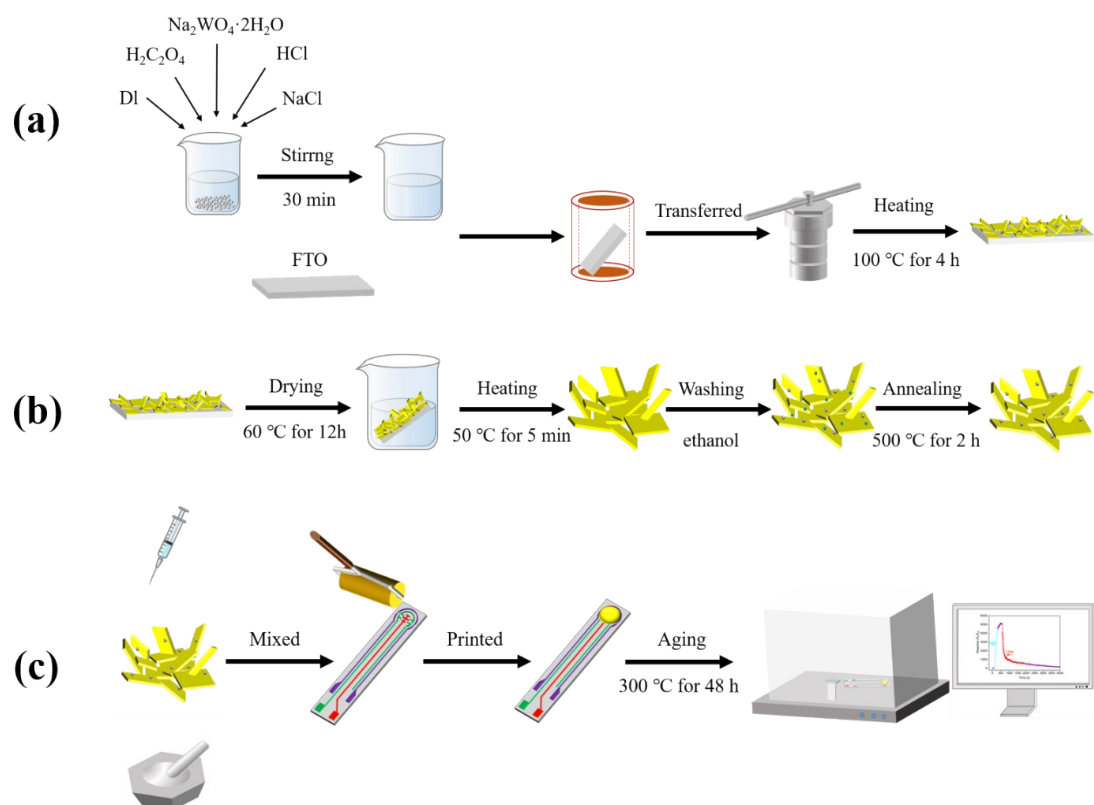


Figure S1. Schematic illustration of the experimental procedure.

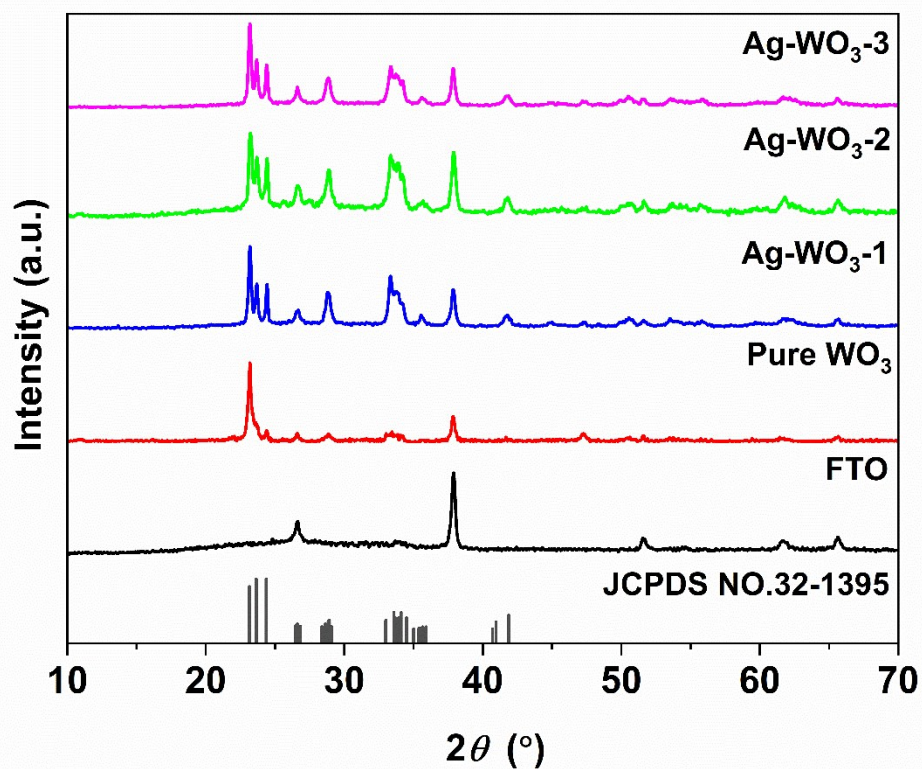


Figure S2. XRD patterns of different samples.

The 2θ peaks at 23.14° , 23.64° , 24.36° , 34.10° and 41.87° , can be attributed to the (002), (020), (200), (202) and (222) crystalline planes of monoclinic γ - WO_3 , respectively. Meanwhile, no obvious characteristic peaks of Ag_2O or Ag are observed for all the samples due to the relatively low Ag content.

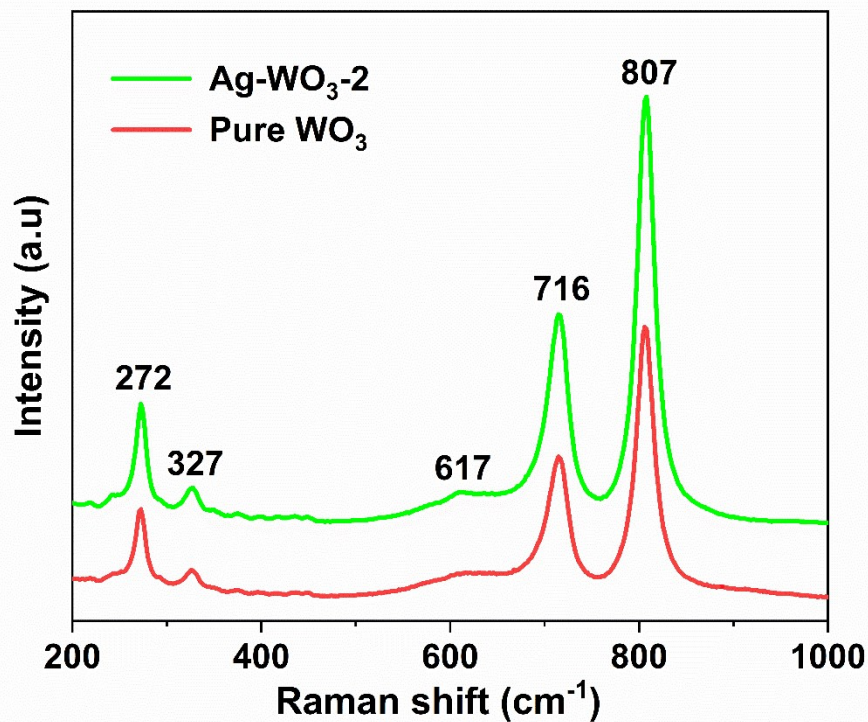


Figure S3. Raman spectra of pure WO_3 and $\text{Ag-WO}_3\text{-2}$.

The peaks at 807, 716, 617, 327 and 272 cm^{-1} are typical characteristic peaks of monoclinic $\gamma\text{-WO}_3$ confirming that WO_3 and $\text{Ag-WO}_3\text{-2}$ are mainly crystallized into the monoclinic $\gamma\text{-WO}_3$ phase. The peak at 807 cm^{-1} , ascribed to the symmetric stretching vibration of the O-W-O bond; the peak at 716 cm^{-1} with a shoulder at 617 cm^{-1} corresponds to the asymmetric stretching vibration of the O-W-O bond; and the peaks at 272 and 327 cm^{-1} are attributed to the bending vibrations of the O-W-O bond.¹⁻

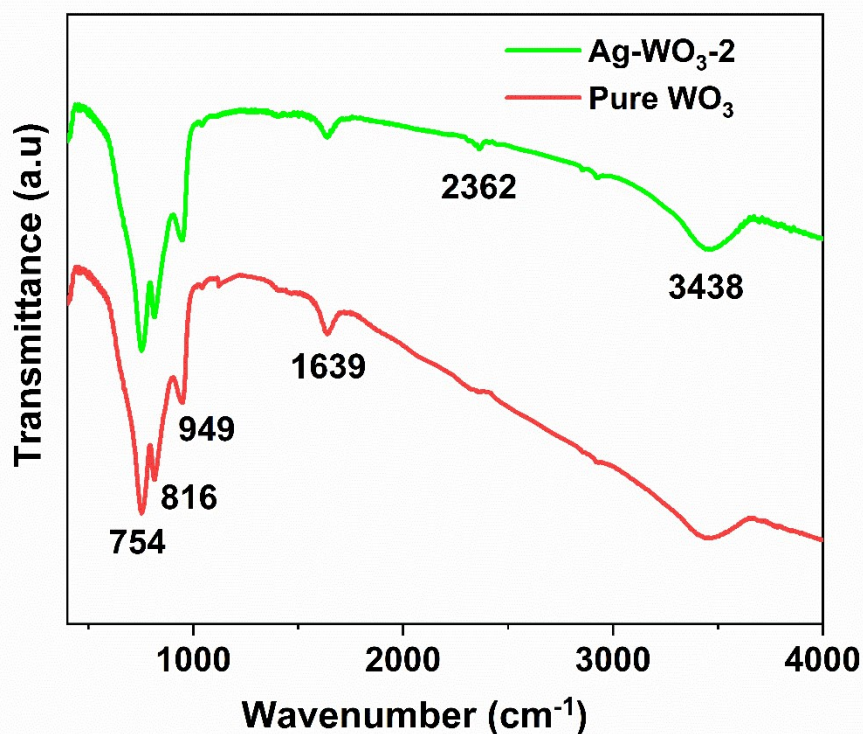


Figure S4. FT-IR reflectance spectra of pure WO₃ and Ag-WO₃-2 in the spectral region between 400 and 4000 cm⁻¹.

The bands at 754 and 816 cm⁻¹ ascribed to the stretching vibration of the W–O–W. Besides, the band at 949 cm⁻¹ can be ascribed to the W=O stretching vibration modes of terminal W–O bonds.^{5, 6} Minor peak at 2362 cm⁻¹ is attributed to CO₂ adsorption on WO₃.⁷ The band at 3438 cm⁻¹ and 1639 cm⁻¹ are derived from the O–H group, indicating that the sample contains water molecules.⁸ Moreover, no obvious position shifts of FT-IR and Raman spectra after functionalized with Ag single atoms, which confirmed that the loading of WO₃ has a negligible effect on its structure.

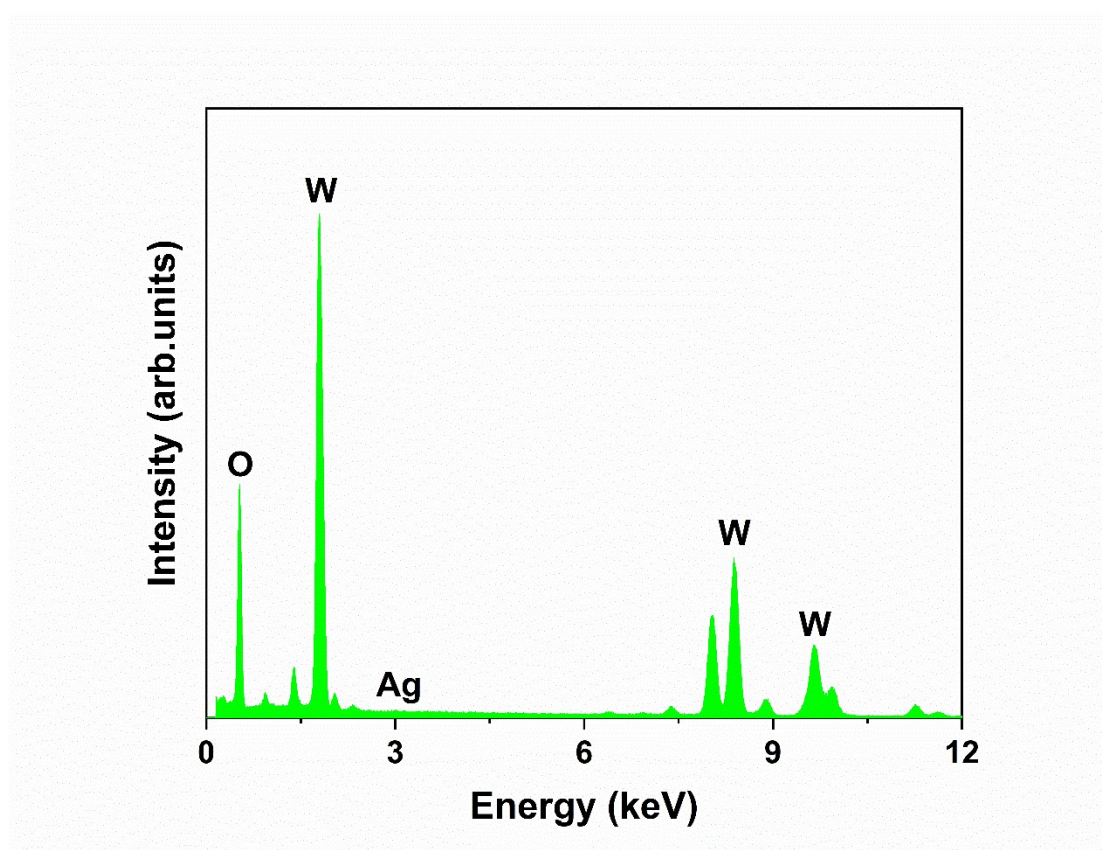


Figure S5. EDS spectra of the Ag-WO₃-2

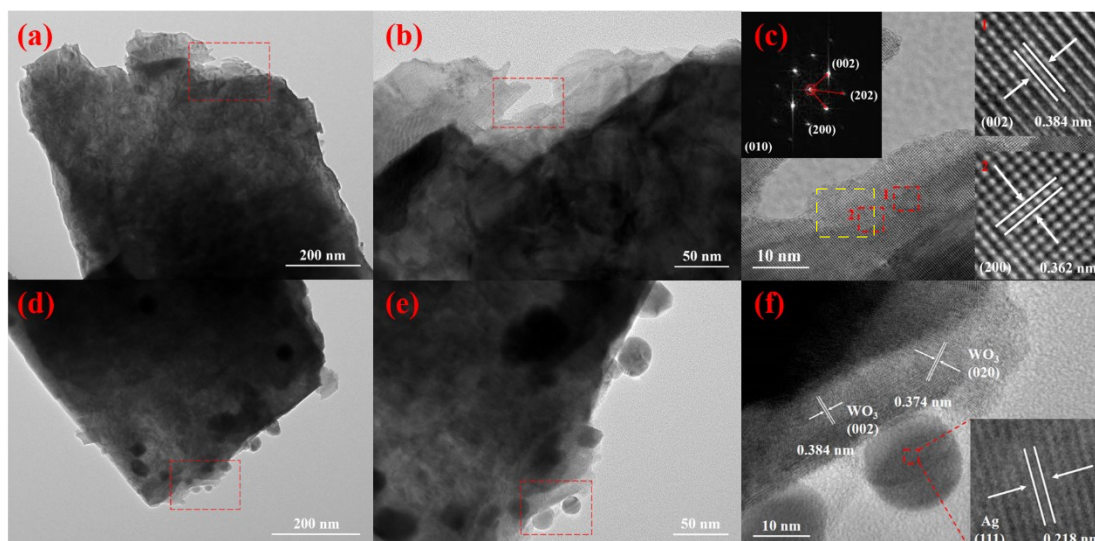


Figure S6. TEM images of (a), (b) and (d) Pure WO_3 with different magnifications. (c) FFT pattern (inset) for (100). (e), (f), and (g) $\text{Ag-WO}_3\text{-2}$ with different magnifications.

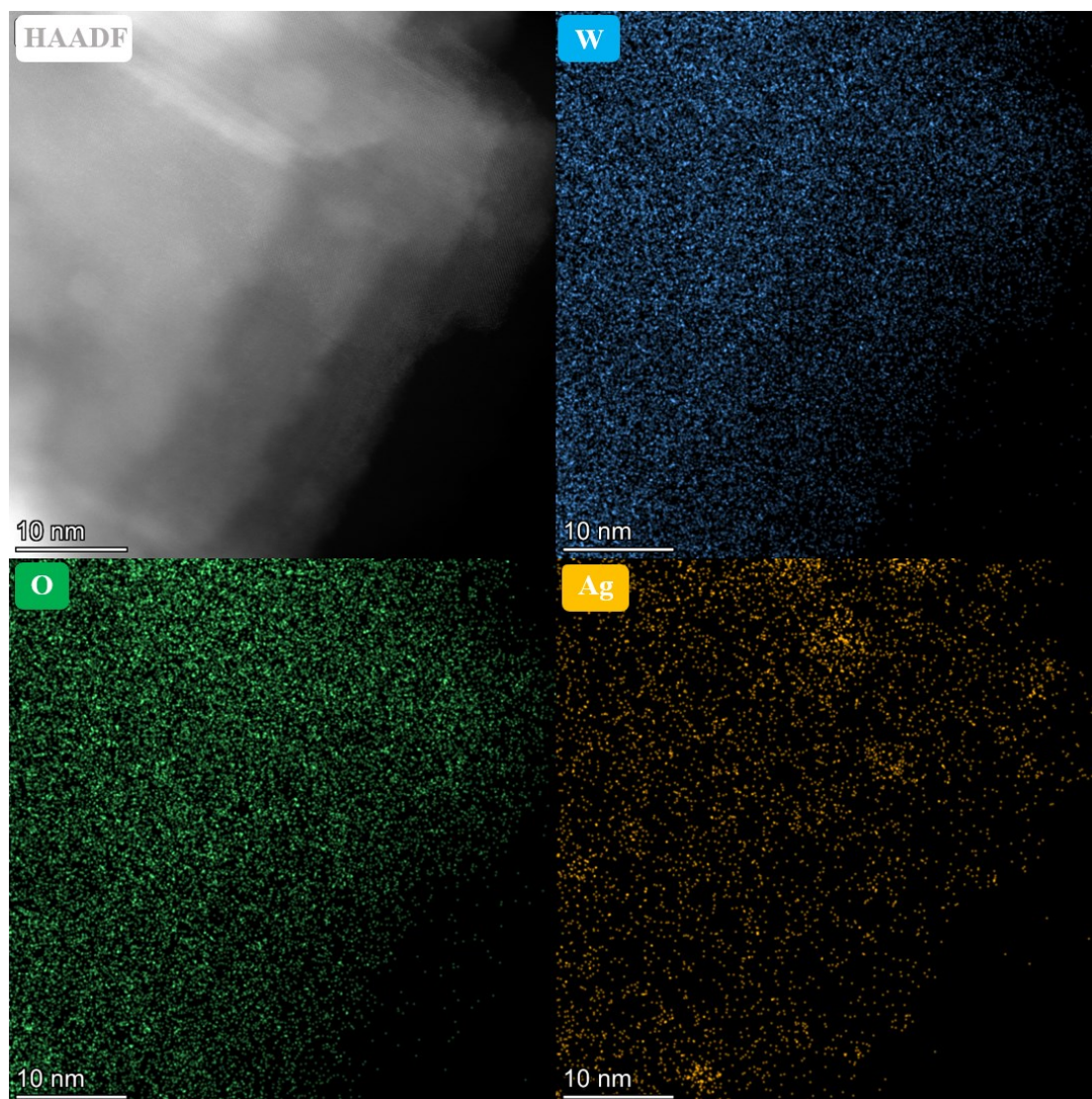


Figure S7. EDS-STEM elemental mapping analysis of Ag-WO₃-2.

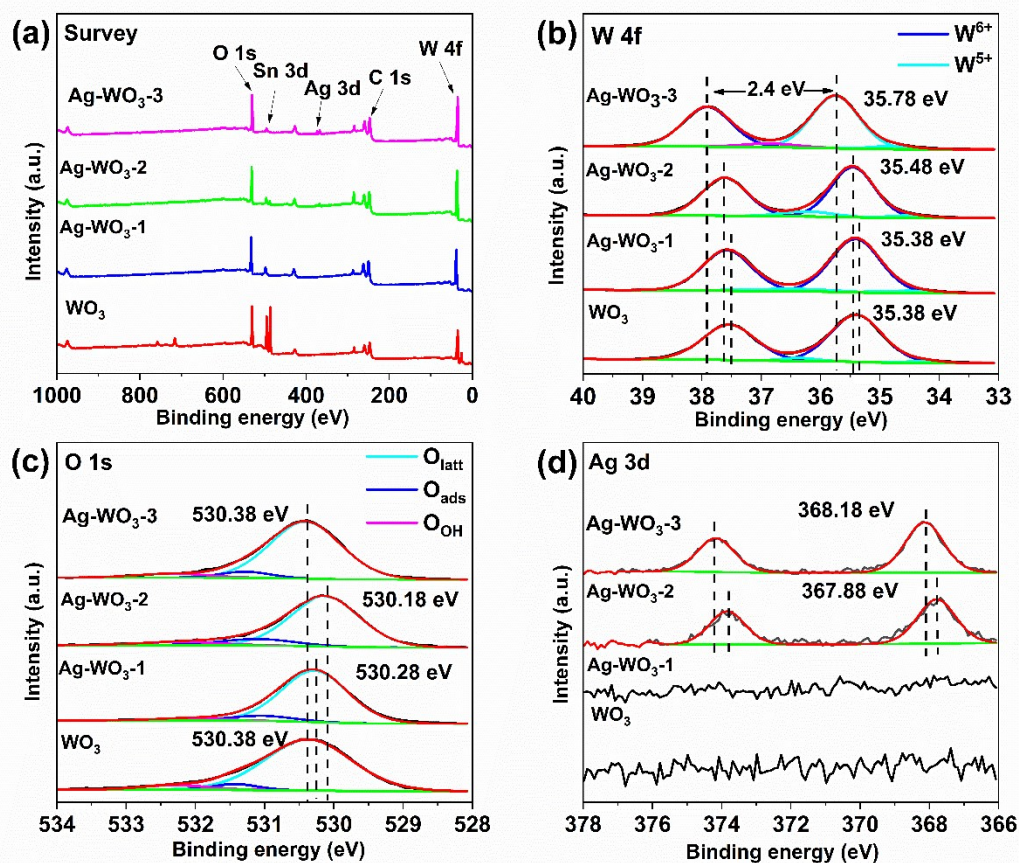


Figure S8. XPS spectra of the samples (a) survey. (b) W 4f. (c) O 1s and (d) Ag 3d.

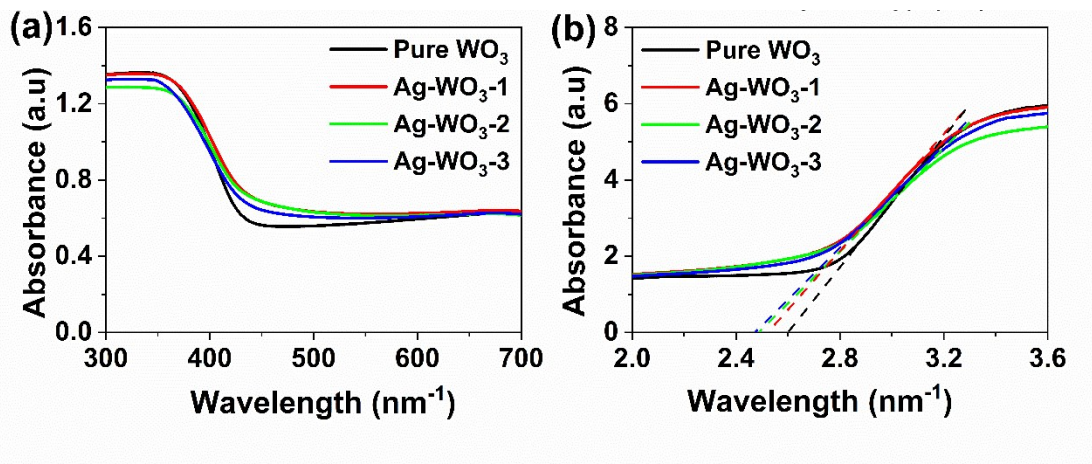


Figure S9. (a) UV-vis diffuse reflectance spectra. (b) plots of $(\alpha h\nu)^2$ vs photon energy $h\nu$ patterns of the samples.

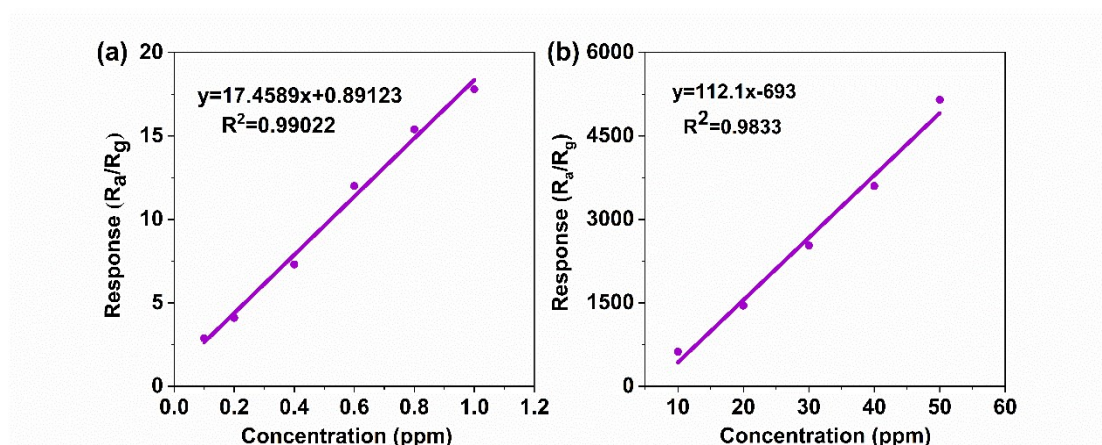


Figure S10. The sensing response showed two different linear relationships to the TEA concentration from (a) 0.1-1 ppm and (b) 10-50 ppm

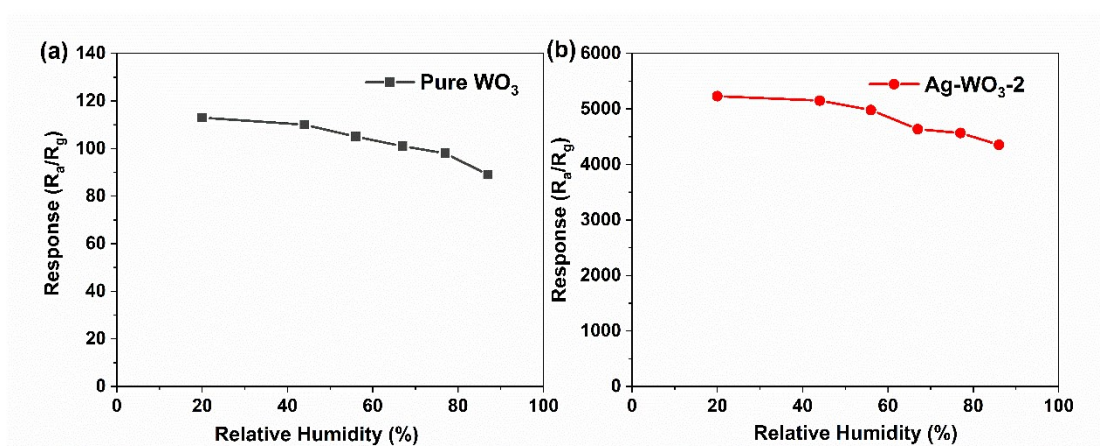


Figure S11. Responses of (a) pure WO_3 to 50 ppm TEA under the RH range from 20% to 90% at 250 °C (b) Ag- WO_3 -2 sensor to 10 ppm TEA under the RH range from 20% to 90% at 175 °C.

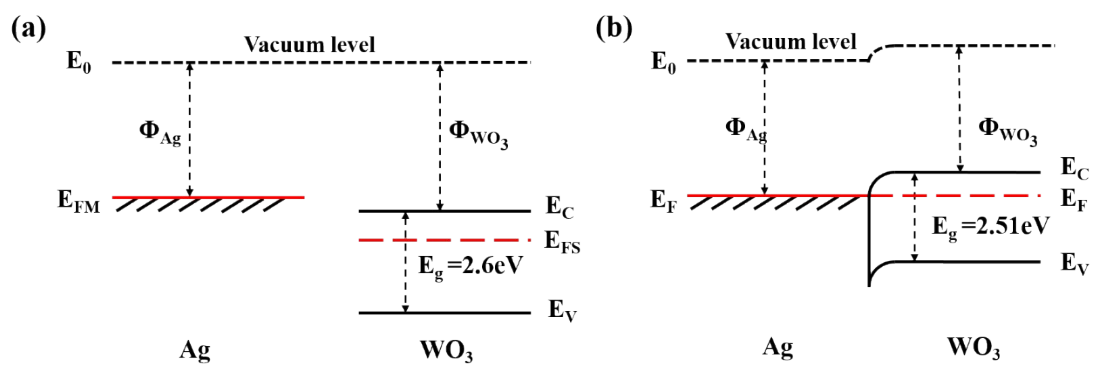


Figure S12. The proposed energy band diagram of Ag- WO_3 at equilibrium (a) before and (b) after contact.

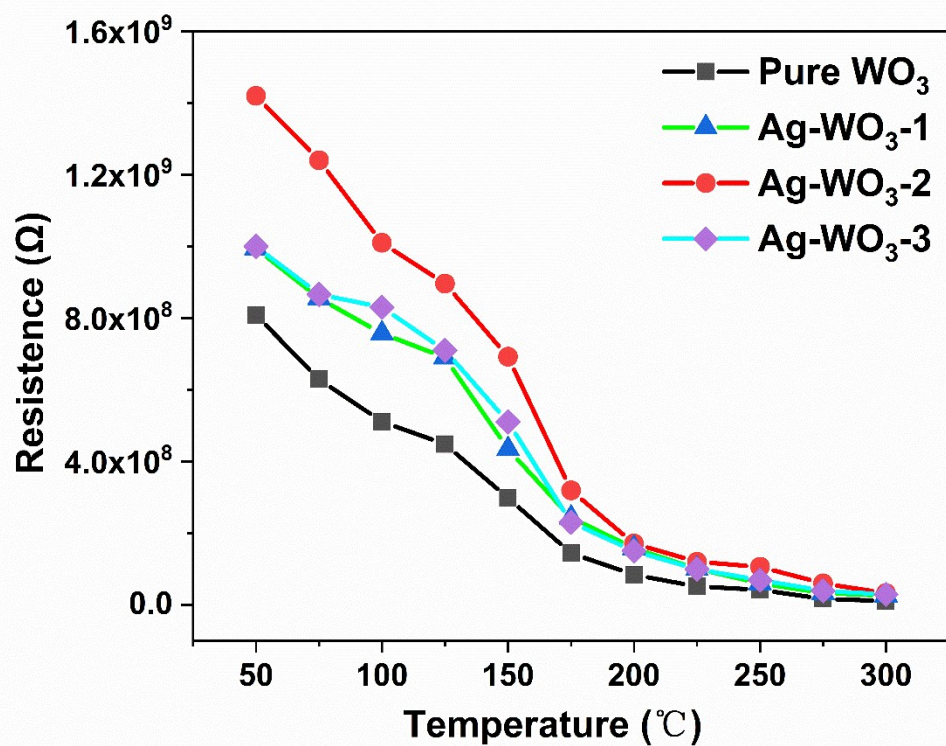


Figure S13. The change in basic resistance of pure WO₃, Ag-WO₃-1, Ag-WO₃-2, Ag-WO₃-3 gas sensors with the operating temperature range from 50 °C to 300 °C.

Table S1. Purities, providers, and CAS numbers of the chemicals.

Chemicals	Purities	Providers	CAS No.
Sodium tungstate dehydrate	AR	Tianjin Zhiyuan Chemical Reagent	10213-10-2
Sodium chloride	AR	Factory	7647-14-5
Ethanedioic acid	AR	Tianjin Fuchen Chemical Reagent Factory	144-62-7
Ethanol	AR	Tianjin Fuchen Chemical Reagent Factory	200-578-6
Silver nitrate	AR	Tianjin Zhiyuan Chemical Reagent	7761-88-8
Hydrochloric acid	AR	Factory	7647-01-0

Table S2. The Ag contents of Ag-WO₃-1, Ag-WO₃-2, Ag-WO₃-3 were measured by XPS.

Sample	Ag-WO ₃ -1	Ag-WO ₃ -2	Ag-WO ₃ -3
Ag content (wt %)	0.02	0.226	0.418

Table S3. Comparison of TEA sensing performance of various materials reported in recent literature.

Materials	Work temperature (°C)	Response/ppm	Response/recovery time (s)	LLD (ppm)	Ref.
WO ₃ NPs	RT	13.6/1000	-	5	9
WO ₃ -SnO ₂	220	87/50	6/7	1	10
Pd-In ₂ O ₃	220	47.56/50	108/117	1	11
Fe-NiO	260	64/50	26/5	1	12
WO ₃	220	16/50	1.5/22	5	13
WO ₃ /Co ₃ O ₄	240	14.5/10	13/152	0.1	14
WO ₃ NRs	250	48/10	-	1	15
Pt-Ce/In ₂ O ₃	180	1050/10	40/236	0.1	16
Pt/SnO ₂	200	136.2/10	3/6	0.007	17
SA-Pt-WO ₃	240	1182/50	20/253	0.03	18
Ag-WO ₃	175	5150/50	189/1380	0.0017	This work

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