Electronic Supplementary Material (ESI) for Dalton Transactions.

Preparation of Pt/WO_3@ZnO hollow spheres for low-temperature and high-efficiency detection of triethylamine

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1. Experimental section

1.1 Synthesis of pure WO_3 nanomaterials

WO_3 was synthesized by the solvothermal method. 1.5 mmol WCl_6 was added to a beaker containing 30 mL ethanol, the mixed solution was stirred for 40 min, then transferred to a 50-mL Teflon-lined stainless steel autoclave and heated at 180°C for 24 h. After cooling to room temperature, the solution was washed with DI water and ethanol alternately. The sample was dried at 60°C and annealed in air at 400°C for 2 h to obtain WO_3 powder, named WZ-0.

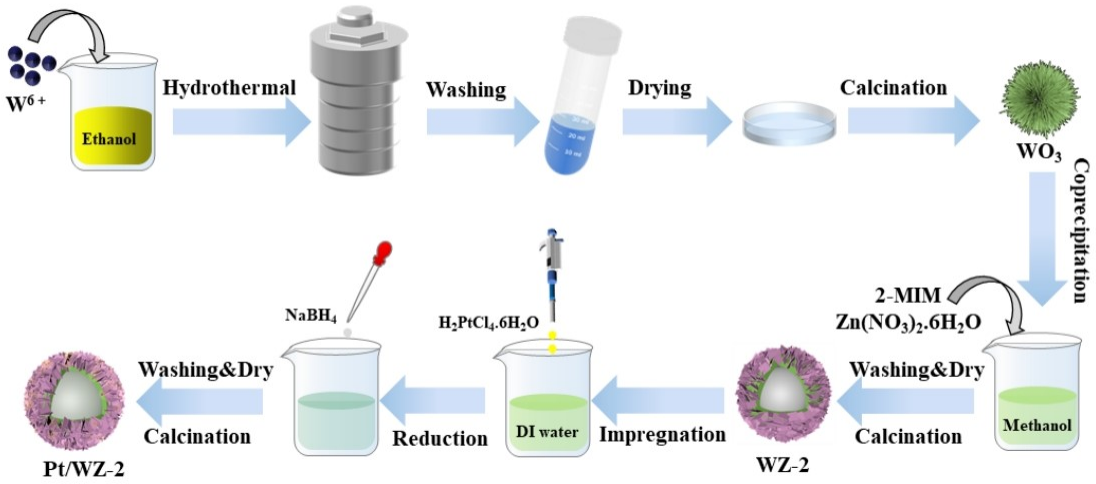

Fig. S1 Preparation process of WZ-0, WZ-2, and Pt/WZ-2 samples.

1.2 Test gas configuration

The test gases are obtained from the corresponding analytical grade liquids configured according to Eq. (1) [1]:

$$C = \frac{22.4 \times \varphi \times \rho \times V_1}{M \times V_2} \times 1000 \quad (1)$$

Where C is the concentration of the gas (ppm), ϕ is the purity of the liquid sample (%), ρ is the density of the liquid sample (g/cm^3), V_1 is the volume of pure liquid injected into the glass bottle for analysis (μL), M is the molecular weight of the liquid sample (g/mol), and V_2 is the volume of the glass bottle (1 L).

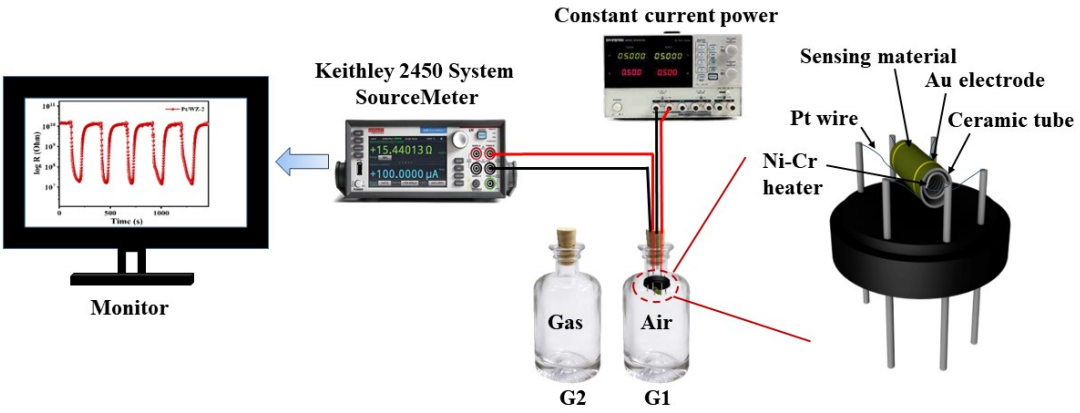

Fig. S2 Schematic diagram of the test system and gas-sensitive element.

When the resistance of the gas-sensitive element in G1 (the resistance in the air is defined as R_a) reaches stability it is quickly transferred to G2 until the resistance (the resistance in the gas to be measured is defined as R_g) stabilizes and is transferred to G1 again, recording the resistance values R_a, R_g, respectively.

1.3 Characterization & Analysis

The reflectance spectra in the wavelength range of 250-800 nm were measured with a UV-2600 UV ultraviolet spectrophotometer (Shimadzu, Japan), and the absorbance spectra and band gap widths of the samples were analyzed.

From **Fig. S3**, all samples show strong peaks below 450 nm, which may be attributed to the interband transition of WO_3. The bandgap (E_g) WZ-0, WZ-2, 1Pt/WZ-2 are 2.56, 2.51, 2.38 eV, respectively. The bandgap of the WZ-2 decreased slightly, and the band gap decreased significantly after loading Pt on WZ-2, indicating that both the construction of heterojunction and Pt modification can reduce the energy required for electron transfer.

The XRD and SEM images of the recycled sample 1Pt/WZ-2 in **Fig. S7**. Comparison with the sample before the performance test showed that no new diffraction peaks appeared and the morphology was basically unchanged, indicating that the material is maintained.

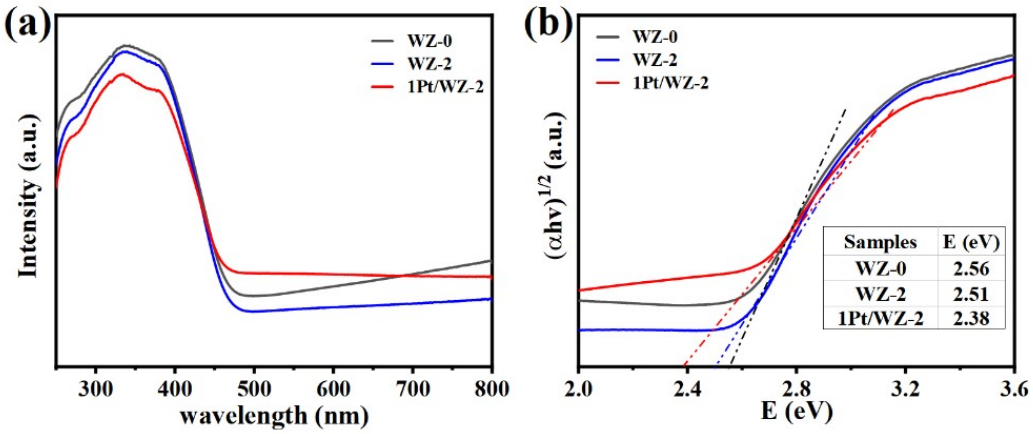

Fig. S3 (a) UV-vis diffuse reflectance spectra, (b) Tauc's plots of WZ-0, WZ-2, 1Pt/WZ-2.

2. Gas sensing performance

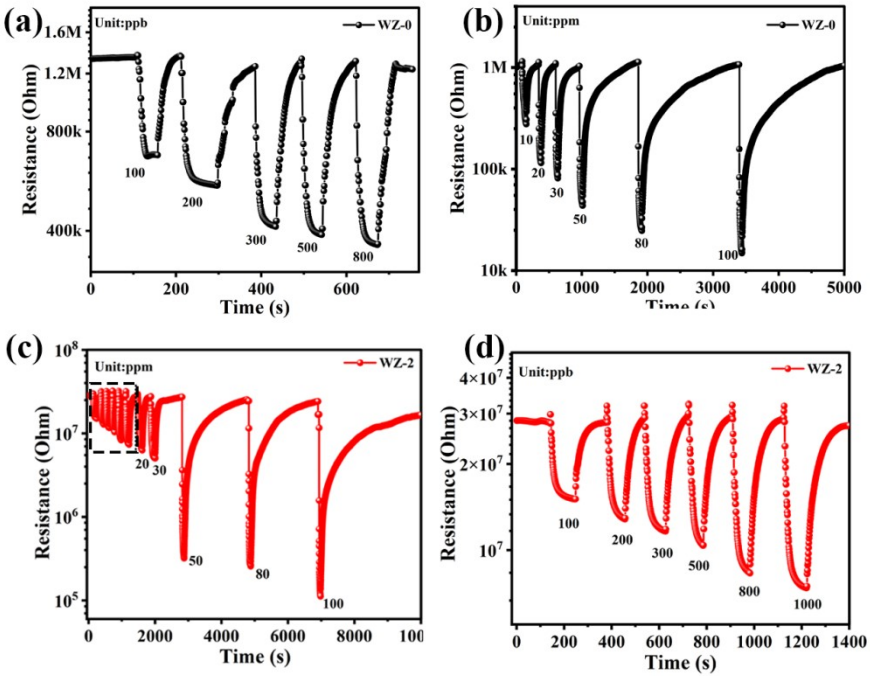

Fig. S4 Concentration-resistance dynamic response curves of WZ-0 and WZ-2.

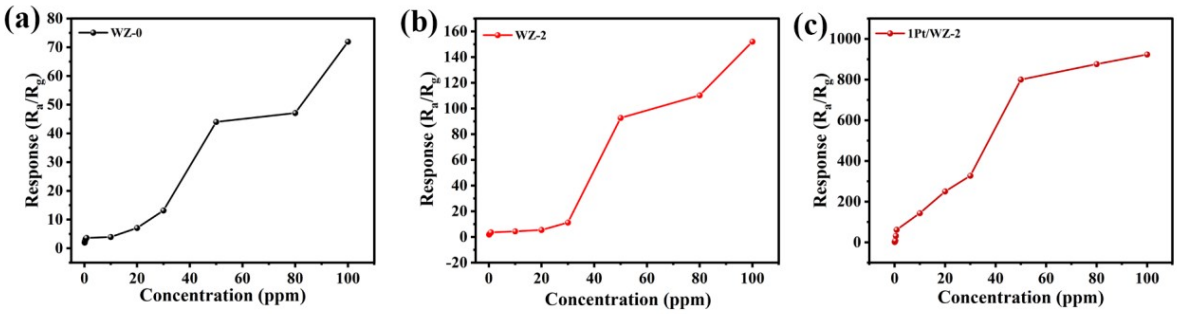

Fig. S5 The responses of WZ-0, WZ-2 and 1Pt/WZ-2 to different concentrations of TEA.

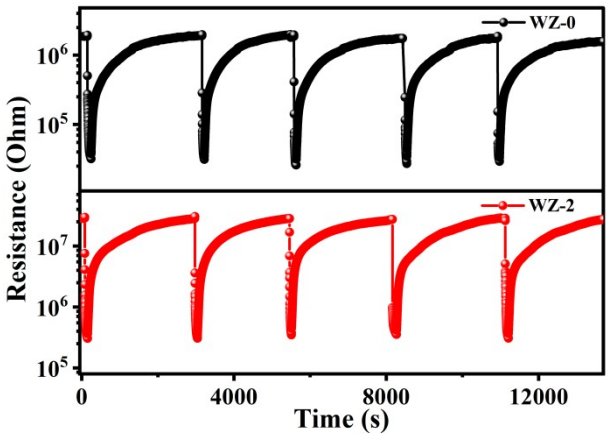

Fig. S6 Repeatability testing of WZ-0 and WZ-2.

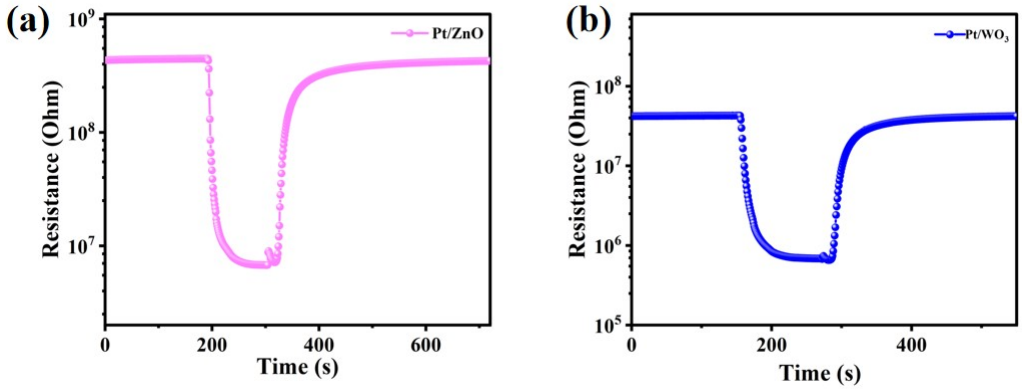

Fig. S7 The response of Pt/WO_3 and Pt/ZnO at optimum working temperature to 50 ppm TEA gas.

Pt/ZnO and Pt/WO_3 were prepared without the addition of WO_3 and ZnO in the preparation of 1Pt/WZ-2, and the responses of Pt/ZnO and Pt/WO_3 for 50 ppm TEA gas were 66 and 57 at the optimum operating temperature of 225°C, which further verifies that the improved sensitivity of the 1Pt/WZ-2 gas is due to the synergistic effect of the heterojunction and the noble metals.

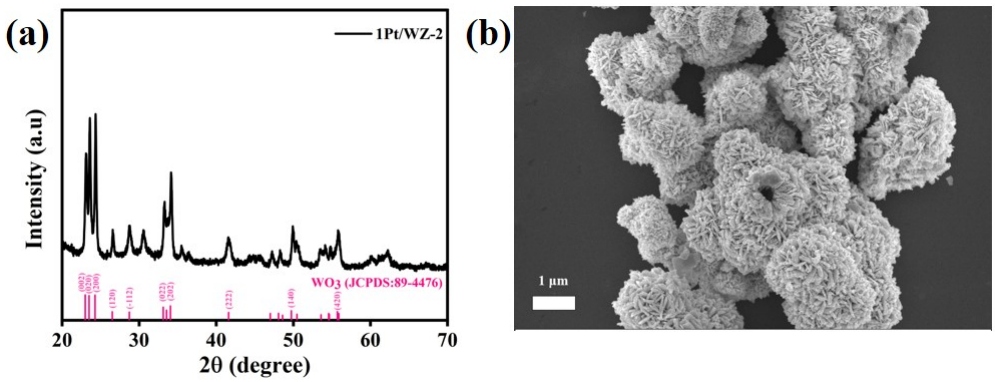

Fig. S8 (a) XRD and (b) SEM images of the recycled sample 1Pt/WZ-2.

A series of gases are emitted during the storage of seafood, and TEA which acts as an important component will gradually increase as the storage time extends [2-4]. Generally, the concentration of TEA released from rotten crucian carp (~200 g) at ambient temperature for 7 days is not higher than 4 ppm [5]. To verify our sensors can be used for the detection of TEA in actual samples, the 1Pt/WZ-2 sensors were used for testing crucian carp stored at different times (0, 3, 6, 12, and 24 h) in a closed environment at room temperature (25°C). The response value of the test is shown in **Fig. S9**. It can be seen from the test results that the response of the sensor is higher as the crucian carp is placed for a longer time. The sensor began to respond significantly (1.5) to crucian carp after 12 h. Li et al. [5] and Hu et al. [6] used a similar approach to evaluate the use of gas sensors in actual sample detection.

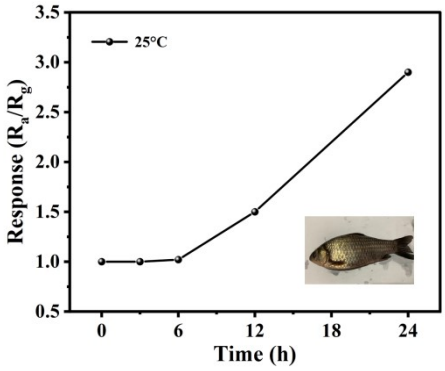

Fig. S9 Response of 1Pt/WZ-2 sensor to the volatiles released from Crucian carp at 25°C

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