

## Supporting Information

### **Controlled evolution of surface microstructure and phase boundary ZnO nanoparticles for the multiple sensitization effects on triethylamine detection**

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## 1. Experimental section

### 1.1 Chemical Reagents

The information of chemicals and the providers are: Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , AR, 99%) and 2-methylimidazole (AR, 99%) is purchased from Sinopharm Chemical Reagent Co. Ltd. Methanol ( $\text{CH}_3\text{OH}$ , 98%) is purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Triethylamine ( $\text{C}_6\text{H}_{15}\text{N}$ , AR, 99.0%) is purchased from Aladdin Industrial Corp. Acetone ( $\text{C}_3\text{H}_6\text{O}$ , AR  $\geq 99.5$ ) is purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Benzene ( $\text{C}_6\text{H}_6$ , AR  $\geq 99.5\%$ ) is purchased from Beijing Bailingwei Technology Co., Ltd. Toluene ( $\text{C}_7\text{H}_8$ , AR  $\geq 99.5\%$ ) is purchased from Luoyang Chemical Reagent Field. Formaldehyde ( $\text{CH}_2\text{O}$ , AR, 37.0% - 40.0%) is purchased from Aladdin Biochemical Technology Co., Ltd. Ammonium hydroxide ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , AR, 25% - 28%) is purchased from Tianjin Fengchuan Chemical reagent Co., Ltd. Anhydrous ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , AR) from Guang fu Technology Co. Ltd. All the chemical reagents of analytical grade are used without further purification. The water used in all experiments is deionized (DI  $\sim 18.2 \text{ M}\Omega \text{ cm}^{-1}$ )

### 1.2 Preparation of ZnO

First of all, 6.7770 g ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and 7.8740 g 2-methylimidazole is dissolved in 100 mL of methanol respectively. The mixture is transferred into a 250 mL round bottom flask and the reaction is carried out in a magnetic stirrer reactor at 60 °C for 24 h. After the reaction temperature is cooled to room temperature, the resulting precipitate is washed for several times with anhydrous ethanol and DI water, and dried

in a vacuum oven for 6 h at 80 °C. These precipitates are calcined at 550 °C, 650 °C and 750 °C in the air for 2 h with a heating rate of 2 °C·min<sup>-1</sup> to obtain the ZnO-550, ZnO-650, and ZnO-750 product respectively.

### ***1.3 Catalyst Characterization***

For X-ray powder diffraction (XRD) experiments on a Rigaku Ultima IV-185, Cu K $\alpha$  radiation is utilized. At room temperature, the scanning angle ( $2\theta$ ) range from 20 - 80° and the scan rate is 10°·min<sup>-1</sup>. The materials micromorphology are examined under a JEM-2100 transmission electron microscope (TEM). The sample's surface is examined using X-ray photoelectron spectroscopy (XPS), which is carried out at Thermo Fisher Scientific with an Al K $\alpha$  X-ray source. All binding energies are calibrated using the carbonaceous C1s line at 284.8 eV as a reference. The optical properties were studied by ultraviolet-visible spectrometer (UV-2450, Shimadzu, Japan). Thermogravimetric analysis (TG) placed the sample in an air atmosphere at 25 – 800 °C, and the heating rate is 10 °C min<sup>-1</sup>, observed the change process of the mass of the sample with temperature or time, and obtained relevant information for instance weight loss ratio, weight loss temperature and decomposition residue. Oxygen programmed temperature desorption (O<sub>2</sub>-TPD) the sample is placed in an oxygen atmosphere at 25 – 900 °C and the heating rate is 10 °C min<sup>-1</sup>, and the adsorption and desorption performance of the catalyst is investigated. Electron paramagnetic resonance (EPR) is a spectral technique for identifying and studying materials with unpaired electrons.

### ***1.4 Testing of humidity***

In gas sensing testing, we use manual sampling methods throughout the entire process. Similarly, for humidity testing, we use a liquid evaporator to convert liquid water into steam by manually injecting deionized water. By using the temperature and humidity sensors included with the instrument, we ensure that the chamber humidity reaches our target humidity. Our target gas, 50 ppm TEA, is then tested at this humidity. In the humidity test, we used a working temperature of 340 °C, and the heating temperature of the evaporator is 150 °C.

### ***1.5 Sensor fabrication and sensing measurements***

The gas sensing properties of the samples are tested by CGS-MT gas analysis system. The performance is evaluated by testing and analyzing the resistance change curve before and after the injection of the target gas. Take a quantity of the prepared sample and pour it into an agate mortar. Then add appropriate amount of ethanol and grind until the sample and ethanol are mixed into a uniform non-granular slurry. The slurry is then uniformly coated on the blank AgPd-VI finger electrode with a coating pen. Next, the prepared sensor is placed in a dryer to completely volatilize the absolute ethanol on the surface of the slurry. Finally, the device is placed in a muffle furnace and calcined at 300 °C for 2 h for aging to obtain a stable sensor component. The tested substrate consists of Al<sub>2</sub>O<sub>3</sub> ceramic substrate and AgPd coating. The length of the interdigital electrode is 13.4 mm, the width is 7 mm, the line width is 0.2 mm, the spacing is 1 mm, and the logarithm is 5 pairs. The resistance between the two points of the electrode is approximately 2 Ω.

During the gas sensitivity test, the coated substrate is placed in a closed chamber with a volume of 20 L. The substrate is heated by adjusting the temperature of the heating table to stabilize its resistance value in air. The target liquid is injected into the chamber with a microinjector, and the target liquid is formed into a certain concentration of gas with the help of an evaporator. At this time, a series of physical and chemical reactions occur when the target gas comes into contact with the surface of the sensing material, and the resistance value of the device increases or decreases significantly. When the resistance value of the substrate is stabilized in the atmosphere of the target gas, the gas mask is opened to desorb the target gas and the resistance returns to the resistance value in air again. When detecting reducing gases, for n-type semiconductors, the response value of the sensor is defined as follows:

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

where  $R_a$  is the resistance value when the sensor is stable in air,  $R_g$  is the resistance value when the sensor is exposed to the target gas.  $S$  represents the sensitivity of the sensor. The response time is defined as the time required for the total resistance of the sensor to change by 90% after the target gas adsorption, and the recovery time is defined as the time required for the total resistance of the sensor to change by 90% after the gas desorption.

**Table S1.** Comparison of the sensing performance of various TEA sensors based on ZnO.

Sensing Materials	OT (°C)	Con (ppm)	Res.	$t_{res}/t_{rec}(s)$	LOD (ppm)	Ref.
<b>2D ZnO nanonets</b>	260	100	213.3	1/5	0.063	<sup>1</sup>
<b>ZnO nanostructures</b>	340	50	30.6	14/11	1	<sup>2</sup>
<b>ZnO rods</b>			60	11/40		
<b>ZnO flowers</b>	280	50	83	8/23	2	<sup>3</sup>
<b>ZnO pyramids</b>			28	13/32		
<b>3D porous ZnO foam</b>	350	100	79.5	1/1	0.09	<sup>4</sup>
<b>ZnO</b>	340	100	30.61	13	1	<sup>5</sup>
<b>Yolk-shell N-ZnO</b>	370	100	133	20/5	1	<sup>6</sup>
<b>Au-loaded ZnO nanorods</b>	40	50	22	11/15	1	<sup>7</sup>
<b>Pt-ZnO microspheres</b>	200	100	242	15/70	8	<sup>8</sup>
<b>PorousAg/AgO/ZnO</b>	240	50	90.3	50/8	1	<sup>9</sup>
<b>ZnS/ZnO porous hollow nanospheres</b>	280	100	31	4/374	1	<sup>10</sup>
<b>MoS<sub>2</sub>/ZnO</b>	200	100	23.57	103/134	1	<sup>11</sup>
<b>ZnO-550</b>			108	8/568	1	This work
<b>ZnO-650</b>	340	50	198	2/420	1	
<b>ZnO-750</b>			101	9/643	1	

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