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Supplementary Information

Synthesis and DFT Study of NH₂-MOF235(Fe)-Derived ZnFe₂O₄-Fe₂O₃- ZnO Multiple Heterojunction Nanocomposites for Triethylamine Gas Detection

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27 1. Material information

28 All the chemical reagents used in the experiments were purchased and used directly without further purification.
29 Dimethylformamide (DMF, ACS reagent, $\geq 99.8\%$) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade,
30 98%) were purchased from Sigma Aldrich (Shanghai) Trading Co. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR, 99%),
31 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$, $> 98\%$), terephthalic acid (PTA, 99%), polyvinylpyrrolidone (PVP, average
32 Mw 58000, K29-32), dimethyl sulfoxide (DMSO, $> 98\%$), and methanol (spectroscopic grade $\geq 99.9\%$) were
33 purchased from Shanghai Aladdin Ltd. Deionized water (resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$) was used in all experiment.

34 All the chemicals used for preparing gases in the subsequent gas sensitivity tests were purchased directly and
35 used without further purification. Formaldehyde (AR, wt% $37.0\% \sim 40.0\%$) was purchased from Liaoning Quanrui
36 Reagent Co., Ltd. Ethanol (AR, wt% $\geq 99.7\%$) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Acetone (AR,
37 $\geq 99.5\%$) and aniline (AR, wt% $\geq 99.5\%$) were purchased from Tianjin Yongsheng Fine Chemical Co., Ltd.
38 Triethylamine (AR, $\geq 99.0\%$) was purchased from Shanghai Aladdin Co., Ltd. Trimethylamine (AR, 30 wt% in H_2O)
39 was purchased from Shanghai McLean Biochemical Science and Technology Co., Ltd. Ammonia (AR, wt% $25 \sim 28\%$)
40 was purchased from Beijing Chemical Industry Factory.

41 2. Heterojunction sample synthesis experiment

42 2.1 Synthesis experiment of $\text{NH}_2\text{-MOF235}(\text{Fe})$

43 Firstly, 50 mL conical flasks were taken out and labeled as A and B. In flask A, 0.55 mmol of ferric chloride
44 hexahydrate and 0.85 mmol of 2-aminoterephthalic acid were dissolved in 15 mL of DMF solution and stirred for
45 15 minutes. Flask B contained 15 mL of ethanol. After stirring flask A for 15 minutes, the solution from flask A was
46 added dropwise to flask B, and stirring was continued for another 15 minutes. These steps were repeated six times.
47 The six solutions were then transferred into 50 mL PTFE liners and placed in a reactor at 85°C for 12 hours. After
48 the reaction, the samples were allowed to cool naturally to room temperature. The precipitates were collected
49 and washed three times with deionized water and anhydrous ethanol, respectively. Finally, the samples were dried
50 in a constant temperature oven at 60°C for 10 hours, resulting in the synthesis of the Fe-MOF precursor for further
51 preparation.

52 2.2 Synthesis of $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3\text{-ZnO}$ multi-heterojunction nanocomposites

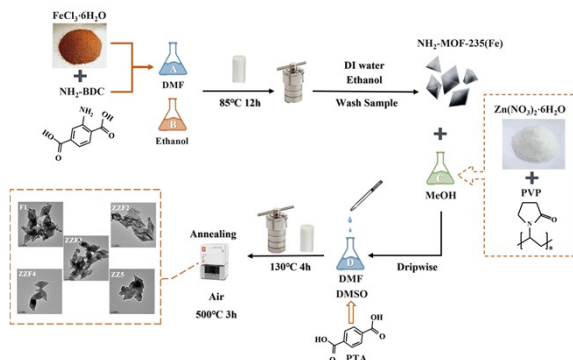


Fig. S1 Schematic of the experimental synthesis of $\text{NH}_2\text{-MOF235(Fe)@MOF5}$ MOF-on-MOF derived multiple heterojunction nanocomposites.

53 0.1g of Fe-MOF precursor, prepared from the above experiments, was dispersed in 10 mL of methanol solution
54 in a conical flask labeled C. The mass of $\text{Zn(NO}_3)_2$ added was 0.05, 0.16, 0.25, 0.72, and 1.08 g. The samples were
55 labeled as samples numbered F1, ZZ2, ZZ3, ZZ4, and ZZ5, respectively. To each samples No. F1-ZZ5, 0.1 g of PVP
56 was added and stirred for 15 minutes. Subsequently, five portions of 3.3 mmol of PTA were dissolved in a mixture
57 of 20 mL of DMF and 10 mL of DMSO in a conical flask labeled D and stirred for 15 minutes to obtain five portions
58 of the PTA solution. At the end of stirring, the PTA solution was added dropwise to the F1-ZZ5 sample solution,
59 stirred for 15 min and then kept at room temperature for 45 minutes. Subsequently, the F1-ZZ5 sample solutions
60 were then transferred into 50 mL of PTFE liners and placed in a reactor at 130°C for 4 hours. After the reaction, the
61 samples were cooled naturally to room temperature, the precipitates were collected and washed three times by
62 centrifugation in deionized water and anhydrous ethanol, respectively. After washing, the samples were dried in a
63 constant temperature drying oven. Finally, the products were annealed in a muffle furnace at 500°C for 3 h to
64 obtain samples F1-ZZ5. The experimental synthesis schematic is shown in Fig. S1, thus completing the synthesis of
65 $\text{NH}_2\text{-MOF235(Fe)@MOF5}$ MOF-on-MOF derived $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3\text{-ZnO}$ ternary heterojunction nanocomposites.

66 3. Fabrication of sensors

67 The sensor consists of a heterojunction material with a ceramic substrate, schematically shown in Fig. S2. The
68 ceramic substrate has a total size of about 1.5×1.5 mm and is made of sintered alumina. The surface of the
69 measuring electrode is plated with gold to increase conductivity. Firstly, an appropriate amount of powdered
70 sample was added the mortar and pestle, assisted by the addition of an appropriate amount of deionized water to
71 form a paste. Pt conductors were soldered to the substrate, and the material was coated onto the inter-finger
72 electrode on the surface of the ceramic substrate.

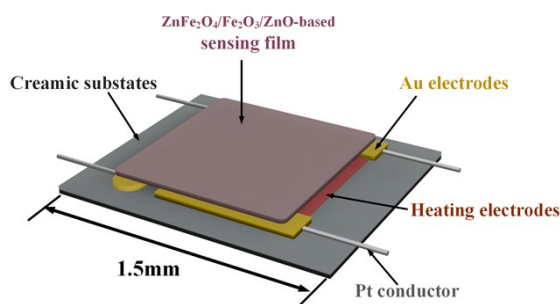
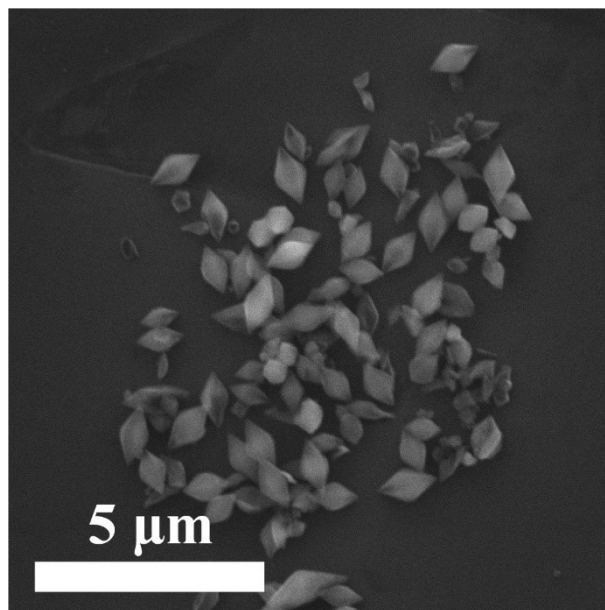


Fig. S2 Schematic diagram of ceramic substrate sensor for gas sensitive test.

73 **4. Material characterization apparatus**

74 XRD data acquisition and material composition analysis of the heterogeneous junction sensing materials was
75 performed using a SHIMADZU LabX XRD-6100 X-ray diffractometer (XRD) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$).
76 Raman spectra of the samples were obtained using a Horiba LabRAM HR Evolution instrument to observe the
77 intermolecular vibrations and provide information on the phases and structures of the samples. The micro-scale
78 morphology and structure of the materials, as well as the distribution of elements, were characterized by TESCAN
79 VEGA4 tungsten filament scanning electron microscopy (SEM) and EDS surface scanning. The nanoscale
80 morphology of the samples was observed using a FEI Tecnai F20 transmission electron microscope (TEM) to obtain
81 both TEM and high-resolution transmission electron micrographs (HRTEM). X-ray Photoelectron Spectroscopy
82 (XPS) were obtained using an ESCALAB MKII to visualize the elemental composition and chemical states of the
83 samples. The optical properties and defects of the samples were analyzed by UV-vis spectroscopy with a Hitachi
84 U4150 and photoluminescence (PL) spectroscopy with an Edinburgh FLS1000.



86

87 **Fig. S3** Polyhedral rhombic SEM of NH₂-MOF235(Fe) without the addition of Zn compounds.88 **6. Elemental weight (Table S1) and atomic percentages (Table S2) obtained by EDS scanning Mapping****Table S1.**

Percentage of weight fraction (wt%) of EDS scanned Fe, Zn, O elements in each sample.

Sample	F1	ZZF2	ZZF3	ZZF4	ZZ5
Fe	69.4 wt%	52.4 wt%	59.3 wt%	13.9 wt%	9.7 wt%
Zn	0.3 wt%	20.0 wt%	12.4 wt%	67.5 wt%	72.6 wt%
O	30.3 wt%	27.6 wt%	28.3 wt%	18.6 wt%	17.7 wt%

Table S2.

Percentage of atomic fractions (at%) of EDS scanned Fe, Zn, O elements in each sample.

Sample	F1	ZZF2	ZZF3	ZZF4	ZZ5
Fe	39.4 at%	31.6 at%	37.0 at%	9.9 at%	7.2 at%
Zn	0.0 at%	10.3 at%	5.9 at%	40.7 at%	46.4 at%
O	60.6 at%	58.1 at%	57.1 at%	49.4 at%	46.4 at%

90 7. XPS

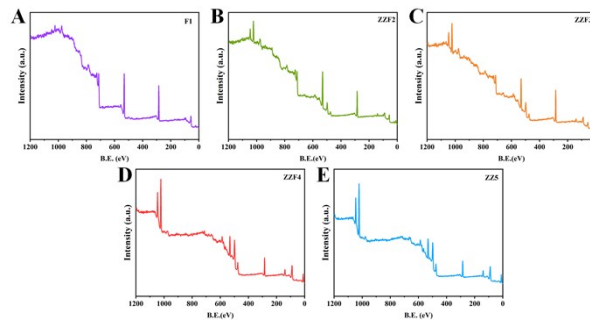


Fig. S4 XPS full test energy spectrum of the sample.

91 8. DFT calculation details

92 All first-principles density functional theory (DFT) calculations were conducted using the Vienna Ab-
93 initio Simulation Package (VASP) ¹⁻³. The Perdew-Burke-Ernzerh (PBE) in the generalized gradient
94 approximation (GGA) with the on-site Coulomb Repulsion U term was applied to describe the exchange-
95 correlation function ^{4,5}. In this work, U(Zn)=5.0 eV and U(Fe)= 3.5 eV for all the calculations. Based on
96 the plane wave method, the projector augmented-wave (PAW) method with an energy cutoff of 400
97 eV was implemented for the electron-ion interactions ^{6,7}. The van der Waals interaction was taken into
98 account using DFT-D3 method with Becke-Jonson damping dispersion correction. All structures were
99 fully relaxed until the electronic energy and force acting on atom were smaller than 10⁻⁴ eV and 0.05
100 eV·Å⁻¹, respectively. The Brillouin-zone sampling was conducted using Monkhorst-Pack (MP) grids of
101 special points with the separation of 0.04 Å⁻¹. A Gaussian smearing of 0.05 eV was applied to speed up
102 self-consistent field iteration. A vacuum height of >15 Å along the vertical direction was selected to
103 avoid the unwanted interaction between the slab and its period images. The optimized structures were
104 illustrated with VESTA software ⁸.

105 8.1 Ball-and-stick structure models

106 After the original cell models of Fe₂O₃, ZnO, and ZnFe₂O₄ surface were established, the structures
107 were optimized, and the crystal faces of different components were matched and optimized. The model
108 of no adsorbed gas was established by matching the (001) face of Fe₂O₃ with the (001) face of ZnO,
109 (111) face of ZnFe₂O₄ with the (001) face of Fe₂O₃, (111) face of ZnFe₂O₄ with the (001) face of ZnO.

110 8.2 Details of adsorption energy calculation

111 The adsorption energy indicates the energy change of the gas molecules during the adsorption

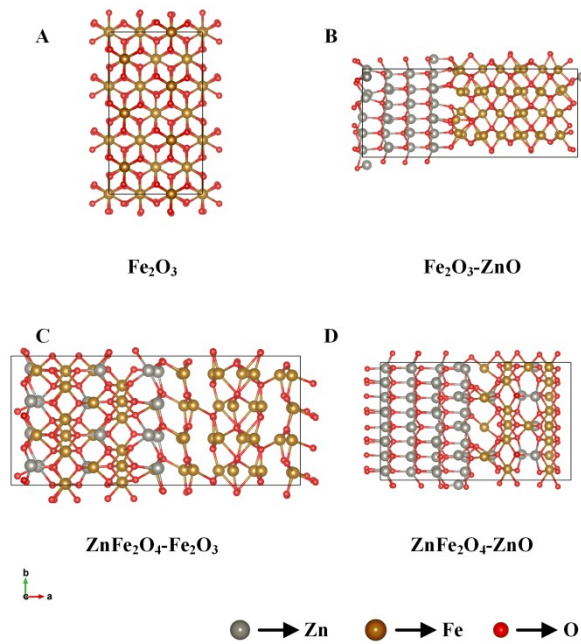


Fig. S5. Structural modeling of Fe_2O_3 and the three types of heterojunctions molecules.

112 process, which is calculated by Equation S1⁹. Among them, E_{total} is the total energy of the gas molecules
 113 after adsorption on the surface of the material, $E_{surface}$ indicates that it is the energy of the surface of
 114 the material, and E_{gas} indicates the energy of the gas molecules.

$$115 \quad E_{ads} = E_{total} - (E_{surface} + E_{gas}) \quad (S1)$$

116 9. Heterogeneous junction gas sensitization mechanism and details of EDL.

117 The gas-sensitive mechanisms are primarily attributable to the thickness-control model of the
 118 surface depletion layer, also known as the grain-boundary barrier model. ZnFe_2O_4 , Fe_2O_3 , and ZnO are
 119 n-type semiconductors, where the main carriers are free electrons. The sensitization process and
 120 mechanism of multiple heterojunction-based gas sensors is investigated by studying the electronic
 121 properties of the multiple heterojunction materials in an atmospheric environment. Redox on the
 122 sample surface involves the adsorbed oxygen negative ions reacting with TEA, releasing the trapped
 123 electrons back into the material's conduction band. Consequently, the depletion layer is lowered, and
 124 the return of free electrons reduces the thickness and height of the potential barriers, resulting in a
 125 decrease in the resistance of the material. At higher temperatures, the enhancement of the sensor
 126 material's surface activity and the consumption of adsorbed oxygen leads to the transport of oxygen
 127 negative ions through the lattice of the material. The lattice oxygen can be directly converted into
 128 surface oxygen vacancies by reacting with reducing gases, thereby increasing the material's reactivity.

129 Multiple heterojunctions can provide a more complex mechanism for the regulation of energy band
130 structure, with the modulation of different ratios of Fe and Zn to form heterojunctions with altered
131 ratios.

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