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Supplementary Information

An enhanced acetic acid sensing of MOF-derived α -Fe₂O₃/ZrO₂ arising from phase junction and defects

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Preparation of reduced graphene oxide (rGO)

GO was prepared from graphite powder following the modified Hummers method, and then reduced graphene oxide (rGO) was obtained through thermal reduction of GO. Firstly, graphite flakes and KMnO₄ were added to the condensed mixed solution of H_2SO_4 and H_3PO_4 , and stirred for 12 hours at 50 °C. After the mixture was cooled to room temperature, it was slowly added to 100 mL of ice water containing 50 mL of 30% H_2O_2 , and the reaction was completed to produce a golden yellow solid. Subsequently supernatant was decanted and the remaining solid was centrifuged using concentrated hydrochloric acid and ethanol several times. The product was dispersed in 200 mL of ether, and filtered with a polypropylene membrane to obtain a yellowbrown solid, which was then freeze-dried. After drying, GO was obtained.

Reduced graphene oxide (rGO) was synthetized through thermal reduction of GO. 200 mg of GO was mixed with water (160 mL) and sonicated for 1 hour. Then, 5% Na_2CO_3 solution was added to the above solution to adjust pH and stirred at 90 °C under reflux for 9 hours. Finally, the NaBH₄ was added to the flask and the mixture was stirred for 3 h in an oil bath at 80 °C. Then, the product was washed several times with deionized water, filtered through a polyamide membrane (pore size 0.2 µm), and dried in a freeze dryer.

Preparation of pristine t-ZrO₂¹. 10 g of ZrOCl₂·8H₂O and 15 g of NH₄Cl were ground in an agate mortar for homogeneous mixing, the mixture was placed into an alumina crucible with a lid and then calcined in a muffle furnace at 550 °C for 4 h. After

being naturally cooled to room temperature, the obtained product was ground into powder as pristine ZrO₂ sample.

Preparation of pristine α -**Fe**₂**O**₃². FeCl₃ · 6H₂O (0.249 g) and terephthalic acid (0.153 g) were dissolved in 10 mL and 5 mL DMF under vigorous stirring, respectively. Then, the FeCl₃ mixed solution was slowly added into terephthalic acid solution. Whereafter, the as-prepared mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and reacted at 120 °C for 16 h. The precipitate was washed with DMF and alcohol several times. Finally, the products were fully dried with vacuum at 120 °C for 12 h, and then calcined at 500 °C for 2 h.

Mott–Schottky (M-S) curves: The α -Fe₂O₃/ZrO₂, saturated calomel electrode (SCE) and Pt wire was used as working electrode, reference electrode and pair electrode, respectively, detected in 0.1 M Na₂SO₄. α -Fe₂O₃/ZrO₂ was evenly mixed with ethanol, and then the paste was dropped on tin fluoride oxide (FTO) glass (1.0×1.0 cm²), and dried at 60 °C. M-S curves were measured voltages of -1.0v to 0.5v versus SCE at frequencies of 100 Hz, 500 Hz, 1000 Hz at room temperature, respectively.

Gas-sensing measurements:



The CGS-1TP directly controls the temperature of the device by external temperature control, so there is no need to make heating wires on the device. The system supports a dynamic gas distribution system and high vacuum pumping, and the measured planar structure sensor substrate can be directly combined with the synthesis process of the material. The CGS-1TP communicates with the computer through the USB interface, collects data in real time and at high speed, and enables direct online analysis of the sensor characteristics. The test process is divided into steps: sample making, connecting samples and test system, setting test conditions, and testing gas sensitivity characteristics (liquid intake mode).

The liquid volume corresponding to the different concentrations of the gas is calculated according to the formula.

$$Q = \frac{V \times C \times M}{22.4 \times d \times \rho} \times 10^{-9} \times \frac{273 + T_R}{273 + T_B}$$

where Q is the volume of the liquid, V is the volume of the test chamber, C is the concentration of liquid vapor, M is the molecular weight of the liquid, d is the purity of the liquid, ρ is liquid density, T_R is room temperature and T_B is the temperature in the test chamber.



Fig. S1 XRD patterns of α-Fe₂O₃/ZrO₂ obtained from ZrFc MOF calcined at different temperatures (a); Response comparison of α-Fe₂O₃/ZrO₂ calcined at different temperatures towards 100 ppm acetic acid (b).

The ZrFc MOF was obtained from ZrCl₄ (0.5 mmol, 0.1166 g), Fc (COOH)₂ (0.5 mmol, 0.1370 g) and AA (25 mmol, 1.4 mL) into the Teflon container containing 15 mL DMF, and heated for 12 hours at 150 °C. Then the ZrFc MOF are calcined at four different temperatures (500, 600, 700, 800 °C) to obtain α -Fe₂O₃/ZrO₂, and performed gas-sensing tests on 100 ppm acetic acid. Resultantly, the α -Fe₂O₃/ZrO₂ calcined at 700 °C shows the optimal gas-sensing property.



Fig. S2 FT-IR spectra of Fe/Zr-x.



Fig. S3 TGA analysis of Fe/Zr-4.



Fig. S4 The repeatability of the Fe/Zr-4.



Fig. S5 Mott-Schotty plots of Fe/Zr-x ((a) 0, (b) 1, (c) 2 and (d) 4) at 100, 500 and 1000 Hz, respectively.



Fig. S6 Tauc plots of Fe_2O_3 (a) and t-ZrO₂(b).



Fig. S7 The XRD patterns of pristine Fe₂O₃ and t-ZrO₂.



Fig. S8 The resistance variation of Fe/Zr-x in acetic acid.



Fig. S9 Mott-Schotty plot of ZrO₂.

Sample	V _m (%)	V _t (%)
Fe/Zr-0	0	100
Fe/Zr-1	66.7	33.3
Fe/Zr-2	72.7	27.3
Fe/Zr-4	88.7	11.3

Table S1 The volume fraction of m-phase and t-phase in Fe/Zr-x.

Table S2 The percentage (%) of reactive oxygen species (O_C and O_V) in Fe/Zr-x.

	Fe/Zr-0	Fe/Zr-1	Fe/Zr-2	Fe/Zr-4
O _V	33	42	55	64
O _C	0	13	15	16
(O _C +O _V)/O _{total}	33	55	70	80

Table S3 The band-gap width of Fe/Zr-x.

	t-ZrO ₂	α-Fe ₂ O ₃	Fe/Zr-0	Fe/Zr-1	Fe/Zr-2	Fe/Zr-4
Band-gap width (eV)	5.07	1.95	2.15	2.11	2.07	2.03

	Fe/Zr-0	Fe/Zr-1	Fe/Zr-2	Fe/Zr-4
E _{CB} (eV) vs SCE	-0.5993	-0.4972	-0.4704	-0.4465
E _{VB} (eV) vs SCE	-2.7493	-2.6072	-2.5404	-2.4765

Table S4 Related E_{CB} and $E_{VB} \, vs$ SCE values of Fe/Zr-x.

Table S5 The slope (m) of M-S curves of Fe/Zr-x at 500 Hz.

	Fe/Zr-0	Fe/Zr-1	Fe/Zr-2	Fe/Zr-4
m	4.6×10^{9}	4 .1 × 10 ⁹	3 .6 × 10 ⁹	3.3 × 10 ⁹

Material	Concentration (ppm)	Sensitivity	Operating temperature (°C)	Response time (s)	Ref.
Mesoporous CuO	100	27.2	200	71	3
In ₂ O ₃ nanofibers	100	28.4	250	25	4
SnO ₂ nanoflowers	100	47.7	260	18	5
SnO_2	100	132	340	11	6
ZnO foam	100	90.37	400	12	7
Mg-ZnO/rGO	100	200%	250	66	8
Pr-doped ZnO	400	8.89	380	37	9
Mesoporous Fe ₂ O ₃	1000	180	150	/	10
$g-C_3N_4-SnO_2$	1000	87.7	185	94	11
Fe/Zr-4	100	61.5	225	28	This work

Table S6 The sensing performances of various materials based acetic acid sensors.

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