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Supplementary Material

The preparation of MOF-derived ZnO/Co_3O_4 nanocages and its sensing performance to H_2S

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Figure and Table Captions:

1. Experimental Section

1.1. Chemicals

All reagents and solvents received from indicated suppliers were used without further purification. All materials were purchased from Sinopharm Chemical Reagent Co. Ltd.

1.2. Characterization

X-ray diffraction (XRD) patterns of the precursor and metal oxides samples were analyzed by using a DX-2700 diffractometer at a rate of 0.03°/s with a copper Kα1 radiation (λ = 1.54056 Å, Hao yuan, Dandong, China). The morphologies of the samples were analyzed by a field emission scanning electron microscope (SEM, FEI Nova Nano SEM 450) and transmission electron microscopy (TEM, JEM-200CX). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of ZnO/Co_3O_4 samples by using an automated gas sorption analyzer (Autosorb-IQ2, Quantachrome Instruments).X-ray photoelectron spectroscopy (XPS) datas were collected using an ESCALAB Xi+ spectrophotometer (UK, Thermo Fischer, ESCALAB Xi+) with Al Kα radiation (hv = 1486.6 eV). The Photoluminescence spectra were measured at room temperature under excitation at 270 nm by a transient steady-state fluorescence spectrometer (Edinburgh Instruments, FLS 1000). The in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) IS-10 Thermofisher Scientific was used to study the reaction mechanism of H_2S. Before the test, the sample was purified with N_2 flow at 120 ºC for 24 h to remove surface impurities and environmental H_2O so that their impacts have been decreased as far as

possible. The background spectrum was collected at 120 ºC. Then, high purity air was introduced into the reactor, after that stream of 10 vol% H_2S in N_2 flow was introduced into the reactor and the DRIFT spectra was collected (20 scans). The H_2S adsorption studies were performed on ZnO/Co_3O_4-500 and pristine ZnO at 120 ºC. The gas sensing tests were studied on the intelligent gas sensing analysis system. (Shanghai Lingpan Electronic Technology Co., Ltd., China)

1.3. Fabrication and measurement conditions of the MEMS gas sensors

The sensors' fabrication is as following: (1) The prepared samples and ethanol were mixed in an agate mortar and dropped onto the MEMS chip's central interdigital electrodes. (2) The MEMS chips were dried at room temperature and sintered at 180 °C for 10 h to improve their stability. (3) Embed the MEMS chips into the intelligent gas sensing analysis system and gas sensing performance were tested. Basic device structure of measuring system is shown in the Fig. S1. The sensors' measurement condition is: (1) The operating temperature of MEMS sensors were controlled by changing the heating voltage. (2) The gas sensor response was tested by a stationary state gas distribution method. A required amount of target gas was extracted from the standard concentration gas bags and injected into the test chamber by a microinjector. The concentration of target gas ($C_{target\ gas}$) was obtained by the formula: $C_{target\ gas} = \frac{V_{target\ gas}}{V_{test\ chamber}} \times C_{bag\ gas}$,where the volume of the test chamber (V test chamber) is 200 cm^3, the concentration of the gas in bag ($C_{bag\ gas}$) is standardized. Hence, we can control the volume of the target gas ($V_{target\ gas}$) extracted from the gas bags by a stationary to get the concentration of target gas. (3) The resistance of MEMS sensor (R_{sensor}) was

calculated by the formula: $R_{sensor=}\frac{(5-V_{out})}{V_{out}}\times R_L$,where 5 is the circuit voltage, V_{out} is the output voltage of the load resistance (R_L) and recorded ten times a second.

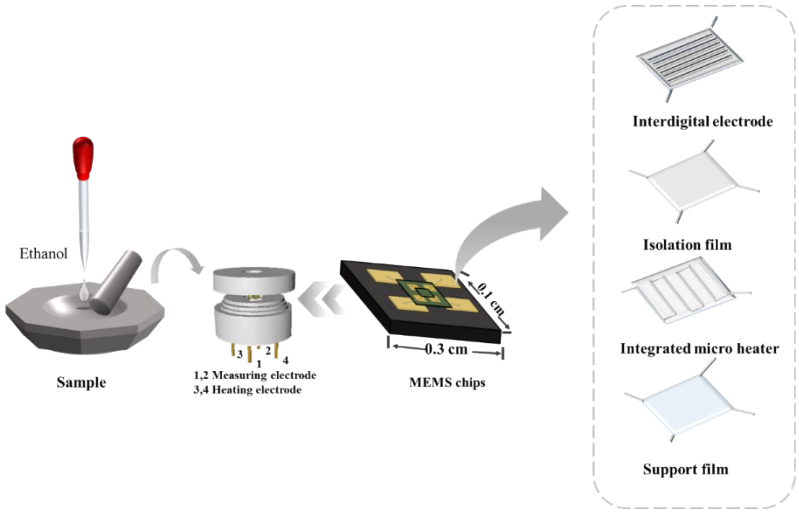

Fig. S1. Structure and manufacturing process of MEMS gas sensor

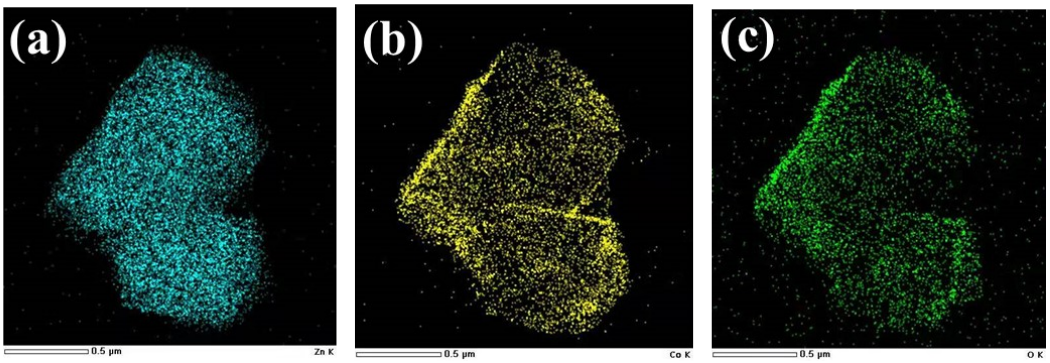

Fig. S2 EDS images of the ZnO/Co_3O_4-500 sample.

Table. S1 The summarization of H_2S semiconductor sensors development.

Sensing materials	Working temperature (°C)	Gas concentration (ppm)	Response	Response/recovery time (s)	Ref.
ZnO/CuO nanoparticles	175	0.8	941	/	[1]
Mo-doped ZnO nanowire	300	5	14	40/50	[2]
ZnO/CuO nanocomposites	250	10	11	58/273	[3]
Cu-ZnO nanomaterials	200	0.2	4733	23/53	[4]
3DIO-Pt/ZnO nanomaterials	320	0.25	11.2	8.7/19/4	[5]
Co_3O_4 nanostructures	225	10	44%	/	[6]
ZnO/PdRh nanocube	260	1	185	18/28	[7]
SnO_2/CuO nanotubes	200	5	1395	5.3	[8]
ZnO/Co_3O_4 nanofibers	270	0.2	/	/	[9]

Table. S2 BET surface areas of different ZnO/Co_3O_4 materials.

Metal oxides semiconductor materials	BET surface area(m^2/g)	Ref.
ZnO/Co_3O_4 composites	17.0	[10]
ZnO/Co_3O_4 microspheres	60.9	[11]
flower-like ZnO/Co_3O_4 nanobundle arrays	37.0	[12]
Co_3O_4 nanoparticle	12.2	[13]
flower-like ZnO/ Co_3O_4 composites	24.9	[14]
ZnO/Co_3O_4 nanoparticle	21.1	[15]
Porous ZnO-Coated Co_3O_4 Nanorod	59.6	[16]
Core-shell structure of ZnO/Co_3O_4 composites	47.4	[17]
ZnO/Co_3O_4-400	78.5	This work
ZnO/Co_3O_4-500	96.5	This work
ZnO/Co_3O_4-600	36.8	This work

Supporting References

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