Electronic Supplementary Material (ESI) for Dalton Transactions.

Extremely Sensitive and Accurate H_2S Sensor at Room Temperature Fabricated with In-doped Co_3O_4 Porous Nanosheets

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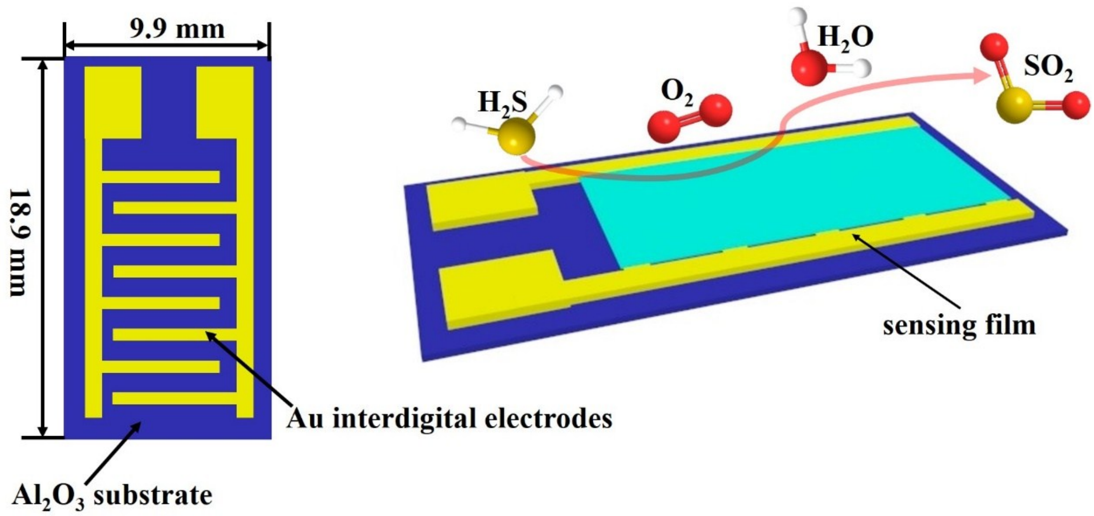

Fig. S1 The interdigitated electrode and gas sensing schematic diagram.

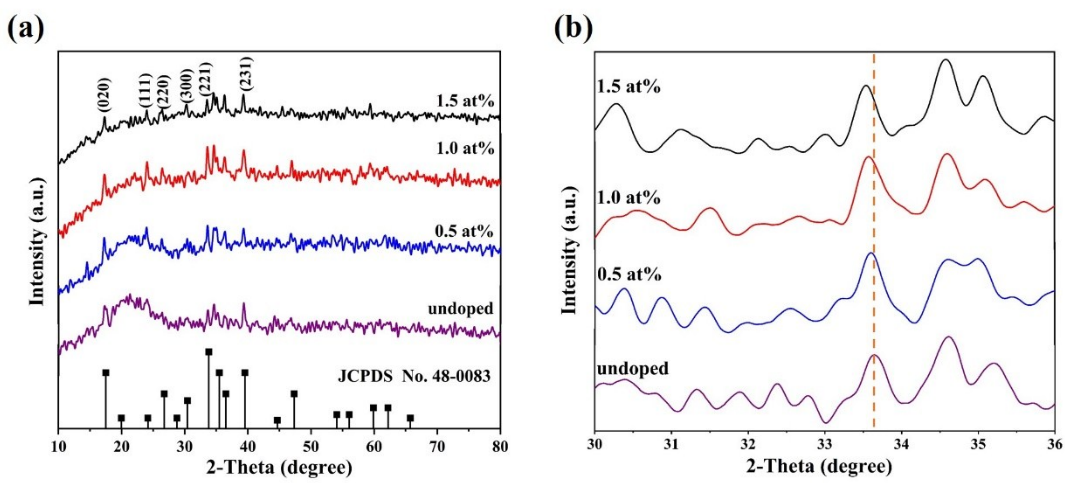

Fig S2. XRD patterns **(a)** and the corresponding partial enlargement of (221) peaks **(b)** of undoped Co_3O_4 precursors and In-doped Co_3O_4 precursors

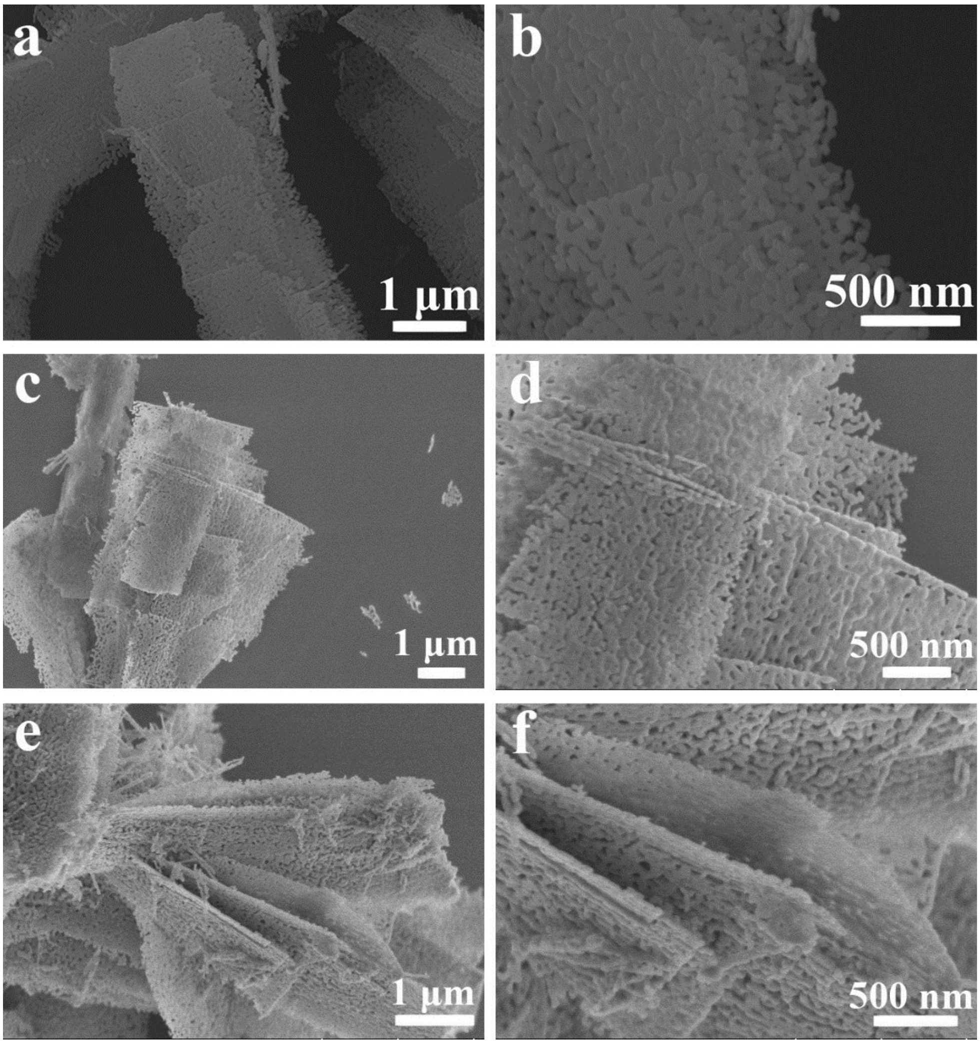

Fig. S3 SEM images of undoped Co_3O_4 (**a**, **b**), 0.5 at% In-doped Co_3O_4 (**c**, **d**) and 1.5 at% In-doped Co_3O_4 (**e**, **f**)

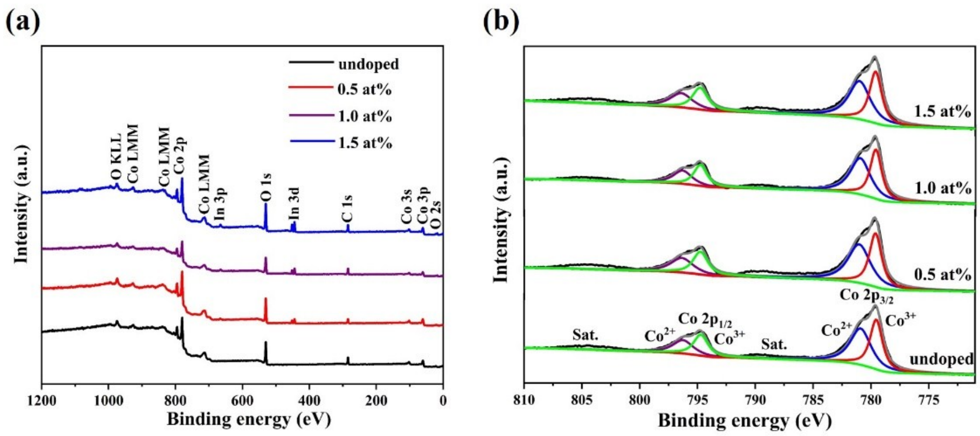

Fig. S4. XPS spectra of the four samples: (a) full-range survey spectra; (b) Co 2p spectra.

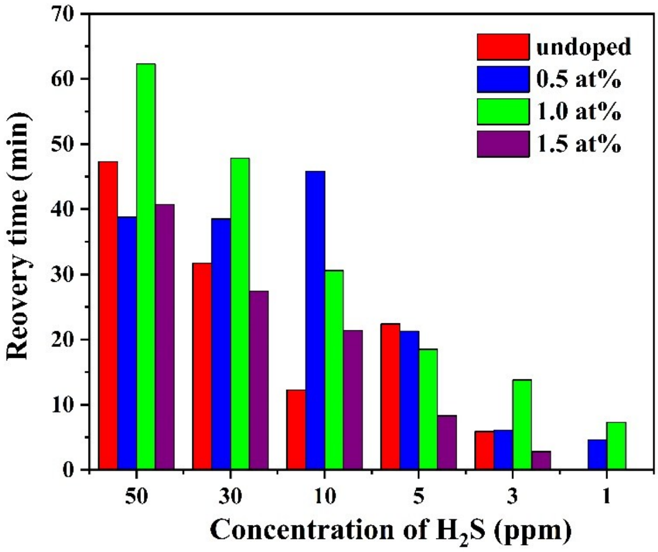

Fig. S5 The relation between the concentrations of H_2S and recovery time.

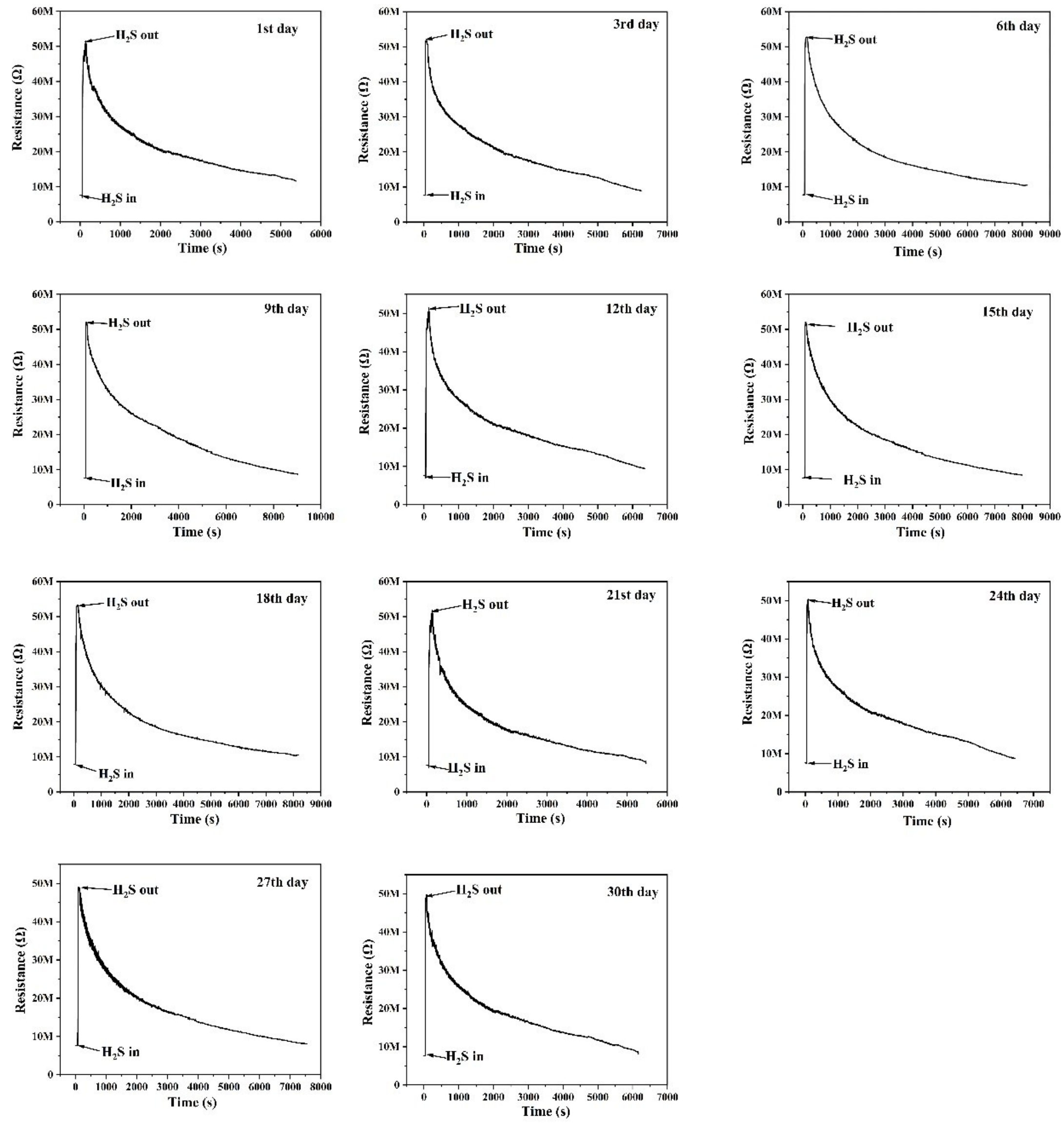

Fig. S6 The long term stability testing curves of the 1.0 at% In-doped Co_3O_4 sensor to 50 ppm H_2S at room temperature for 30 days

Table S1. The lattice constants and microstrains of the four precursors.

Precursors	Lattice constant (Å)			d_{221} (Å)	Microstrain ε (%)
	a	*b*	*c*		
undoped Co_3O_4 precursors	8.8109	10.1596	4.4350	2.6620	0
0.5 at% In-doped precursors	8.8116	10.1606	4.4361	2.6624	0.015
1.0 at% In-doped precursors	8.8122	10.1613	4.3579	2.6629	0.034
1.5 at% In-doped precursors	8.8131	10.1622	4.4399	2.6635	0.056

Table. S2 The results of the response of four samples to different concentrations of H_2S at room temperature.

Samples	50 ppm	30 ppm	10 ppm	5 ppm	3 ppm	1 ppm
undoped Co_3O_4	2.34	1.64	1.44	1.21	1.11	\
0.5 at% In-doped Co_3O_4	5.15	4.72	2.76	1.77	1.35	1.14
1.0 at% In-doped Co_3O_4	6.81	5.92	4.95	3.66	2.46	1.40
1.5 at% In-doped Co_3O_4	2.87	1.87	1.44	1.11	1.04	\

Table. S3 The results of the gas response time of four different samples to different concentrations of H_2S at room temperature.

Samples	50 ppm	30 ppm	10 ppm	5 ppm	3 ppm	1 ppm
undoped Co_3O_4	16 s	22 s	35 s	38 s	55 s	\
0.5 at% In-doped Co_3O_4	13 s	15 s	20 s	17 s	35 s	28 s
1.0 at% In-doped Co_3O_4	9 s	13 s	12 s	21 s	23 s	24 s
1.5 at% In-doped Co_3O_4	13 s	10 s	12 s	24 s	54 s	\

Table. S4 The results of the gas recovery time of four different samples to different concentrations of H_2S at room temperature.

Samples	50 ppm	30 ppm	10 ppm	5 ppm	3 ppm	1 ppm
undoped Co_3O_4	47.3 min	31.7 min	12.3 min	22.4 min	5.9 min	\
0.5 at% In-doped Co_3O_4	38.8 min	38.5 min	45.8 min	21.3 min	6.1 min	4.6 min
1.0 at% In-doped Co_3O_4	62.3 min	47.8 min	30.6 min	18.5 min	13.8 min	7.3 min
1.5 at% In-doped Co_3O_4	40.7 min	27.4 min	21.4 min	8.3 min	2.8 min	\

Table. S5 Properties of the different gas molecules.

Gas name	H_2S	NH_3	NO	$CHCl_3$	HCHO	C_2H_5OH	SO_2
Broken bond	**H**-SH	**H**-NH_2	**N**=O	**H**-CCl_3	**H**-CHO	**H**-OC_2H_5	**S**=O
Bond energy (kJ/mol)	381	450.2	630.6	413.8	368.40	438.1	521.3

The gas sensing reaction involves breaking chemical bonds, which would consume a great deal of energy. And the good selectivity to H_2S may be due to the smaller bond energy of H-SH compared with other target molecules (as shown in **Table S4**).[1,2] H_2S can be decomposed at lower temperature to participate in reaction with sensing material[3,4]. Although the bond energy of HCHO is small to H_2S, interaction strength between the sensing layer and target gas is an effective factor on the sensor response. Co_3O_4 has higher affinity to H_2S as a strong reducing gas compared to other tested gases. This is explained with adsorption of H_2S by Co_3O_4 surface and its decomposition to HS and then to S through the following reaction[3,4]:

$Co_3O_4 + H_2S \rightarrow 3CoO + S + H_2O$

$CoO + H_2S \rightarrow CoS + H_2O$

This reaction is a spontaneous exothermic process, however, the reactions between Co_3O_4 and other target gases cannot do it spontaneously[2]. The exothermic reaction will provide some energy for gas sensing possess, which might be conductive to enhance the response to H_2S.

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3. J. Wang, C. Yang, Y.-R. Zhao, H.-L. Fan, Z.-D. Wang, J. Shangguan and J. Mi, *Industrial & Engineering Chemistry Research*, 2017, **56**, 12621-12629.
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