## **Supporting Information**

## Sulfur Dioxide Gas Sensitive Material Based on Zeolitic Imidazolate Frameworks Derived Carbon

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1. The morphology of synthesized Co-NCNTs and CoZn-NCNTs.

Fig. S1. a, b) SEM images of Co-NCNTs particles. c) SEM image of CoZn-NCNTs particles.

d) TEM image of a CoZn-NCNTs particle hanging on the carbon membrane.



2. Characterizations of the synthesized materials.



Fig. S3. XRD patterns of the synthesized samples, with standard XRD cards included.

The broad peaks in Fig. S3a at ~26° can be attributed to the (002) plane of graphitic carbon. The three peaks located at 44°, 52° and 75° can be attributed to the (111), (200) and (220) planes of metallic cobalt. For CoFe-NCNTs, peaks of Fe<sub>3</sub>O<sub>4</sub> and Fe are also visible. Combined with the EELS elemental mapping results, we can deduce that the exposed metals on the outside of tube shells are removed by the treatment with strong acid, and some metal nanoparticles of Fe, Co, Ni, Cu and Zn enveloped by carbon layers, are remained.



**Fig. S4.** XPS analysis of the CoZn-NCNTs. a) Survey spectrum. Zoomed-in view of b) the Co 2p spectrum and, c) the Zn 2p spectra. Curve fitting of d) the C 1s peak, e) the N 1s peak and, f) the O 1s peak.

The peaks at 778.60 and 793.86 eV in Fig. S4b are assigned to Co  $2p_{3/2}$  and Co  $2p_{1/2}$ , respectively, indicating a binding energy difference of 15.26 eV between Co  $2p_{3/2}$  and

Co 2p<sub>1/2</sub> splitting. Two symmetric peaks centered at 1021.94 and 1044.97 eV in Fig. S4c are assigned to Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$ , respectively, indicating the characteristic spin-orbit split of Zn 2p core level region. The C 1s peak in Fig. S4d is well fit by the convolution of four peaks at 284.6, 285.4, 286.5 and 289.1 eV, assigned to graphitic layers C-C/C=C, C=N, C-O and O-C=O, respectively. Notably, the formation of the C-O bond may arise from the physically adsorbed oxygen on structural defects at the edge of unsaturated carbons induced by the high temperature of pyrolysis, thereby forming oxygen-containing groups when exposed to air.<sup>[1]</sup> The N 1s peak in Fig. S4e is well fit by the convolution of three peaks. The peaks with low binding energy at 398.8 and 400.5 eV correspond to pyridine nitrogen and pyrrole nitrogen, respectively. The pyridinic nitrogen indicate that sp<sup>2</sup> nitrogen bonded to two carbon atoms,<sup>[2]</sup> which is also coordinated to a cobalt or zinc ion. When carbon atoms within the graphene layers are substituted by nitrogen atoms, the peak at 401.6 eV appears, corresponding to graphitic nitrogen. It is worth noticing that the existence of pyridine nitrogen and pyrrole nitrogen is beneficial for the improvement of conductivity by contributing to the p-conjugated system with a pair of p-electrons in the graphene layers. The O 1s core level peak in Fig. S4f with two asymmetric shoulders is well fit by the convolution of four peaks. The peak at 531.5 eV is probably related to OH<sup>-</sup>, and can be associated with the presence of amide and carboxyl compounds. The peak at 532.7 eV relates to oxygen from the chemically or physically adsorbed water, or to oxygen making a single bond with carbon. The peak at 534 eV is probably related to the presence of carbonoxygen double bonds. The complementary peak at 535.5 eV may indicate the presence of compounds containing C-NO<sub>2</sub> groups.



Fig. S5. Raman spectrum of the CoZn-NCNTs.

Raman spectroscopy was performed on the CoZn-NCNTs to examine the degree of graphitization. A broad D peak and a sharp G peak were detected at 1339 cm<sup>-1</sup> and 1595 cm<sup>-1</sup>, respectively, suggesting that the existence of graphitized carbon, which is consistent with the high resolution TEM images.<sup>[3,4]</sup> The D peak relates to the breathing mode of A1 g symmetry involving phonons near the K zone boundary, which is forbidden in perfect graphite and becomes active in the presence of disordered or finite-size crystals of graphite (nano-graphite crystals). The G peak corresponds to the  $E_{2g}$  mode of in-plane vibrations of ideal *sp*<sup>2</sup> carbons.<sup>[5]</sup>

## 3. Gas sensor and the performance.

In order to check the pH stability of synthesized CoZn-NCNTs, we have treated the samples in 1×10<sup>-6</sup> M, 5×10<sup>-6</sup> M, 1×10<sup>-5</sup> M, and 1×10<sup>-4</sup> M sulfuric acid solution and sodium hydroxide solution for 5 h, respectively. In the treatments, 100 mg CoZn-NCNTs was put into 20 mL sulfuric acid solution or sodium hydroxide solution with certain concentration for 5 h. The obtained samples were collected by filtration and dried in oven at 70 °C for 3 h. Then we measured the sensing performance of the treated samples.



**Fig. S6.** XRD patterns of CoZn-NCNTs after treatment by sulfuric acid and sodium hydroxide solution for 5 h, respectively.



**Fig. S7.** Response-recovery curves of CoZn-NCNTs to 30 ppm  $SO_2$  at room temperature, after treatment in sulfuric acid and sodium hydroxide solution for 5 h.



**Fig. S8.** The response of CoZn-NCNTs to 30 ppm  $SO_2$  at room temperature after treatment by sulfuric acid and sodium hydroxide solution.



**Fig. S9.** Dynamic response-recovery curves of the CoZn-NCNTs sensor to 100 ppm  $SO_2$  at room temperature. The reddish arrow marked with 'In' denotes the time when the target gas was flowed in, while the one with 'Out' denotes the time when the target gas was removed.

![](_page_8_Figure_2.jpeg)

Fig. S10. Response-recovery curves of CoZn-NCNTs to 100 ppm  $NH_3$ ,  $H_2$ , and CO at room temperature.

![](_page_9_Figure_0.jpeg)

Fig. S11. Long time-dependent responses of CoZn-NCTNs to 100 ppm  $SO_2$  over one month.

![](_page_9_Figure_2.jpeg)

Fig. S12. Dynamic response-recovery curves of CoZn-NCNTs sensor to 30-1000 ppm  $SO_2$  at room temperature.

![](_page_10_Figure_0.jpeg)

**Fig. S13.** Response-recovery curves (red) of the sensor based on physical mixture of Co-NCNTs and Zn-NCNTs (mass ratio 1:1) to 100 ppm  $SO_2$  at room temperature. The response-recovery curves (gray) of only CoZn-NCNTs is also included for comparison.

![](_page_10_Figure_2.jpeg)

Fig. S14. Response-recovery curve of the CoZn-NCNTs sensor to 50 ppm NO<sub>2</sub> at room

temperature.

![](_page_11_Figure_0.jpeg)

Fig. S15. The electronic band structure of pristine nanotube (10,0) without (a) and with

(b) SO<sub>2</sub> adsorption.

Sample/Elements (Mass%)	Со	Ni	Fe	Cu	Zn
CoNi-NCNTs	9.72	0.17	١	١	١
Co-NCNTs	17.58	١	١	١	١
CoFe-NCNTs	18.36	١	6.22	١	١
CoCu-NCNTs	7.17	١	١	0.1	١
CoZn-NCNTs	11.94	١	١	١	1.92

Table S1 Metal contents in Co-NCNTs and CoM-NCNTs using ICP-OES.

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