

## Supporting Information

### Preparation of Porous $\text{Co}_3\text{O}_4$ and its Response to Ethanol with Low Energy Consumption

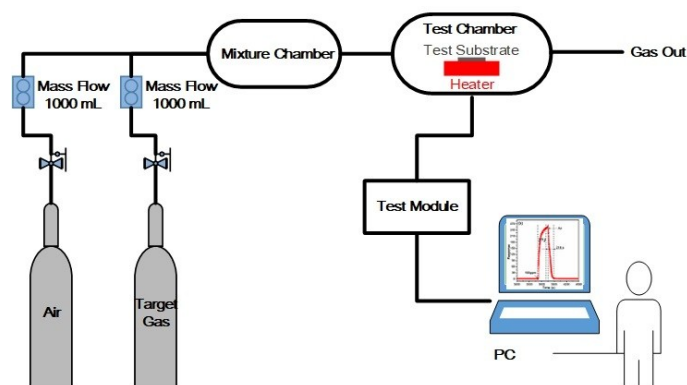
*Xiao Zhang,\*<sup>a,b</sup> Yaohua Xu,<sup>a,b</sup> Hao Liu,<sup>a,b</sup> Wenrui Zhao,<sup>a,b</sup> Anjie Ming,<sup>a,b</sup> and Feng Wei<sup>a,b</sup>*

<sup>a</sup> State Key Laboratory of Advanced Materials for Smart Sensing, General Research Institute for Nonferrous Metals, Beijing 100088, China. Email: zhangxiao@grinm.com

<sup>b</sup> GRIMAT Engineering Institute Co., Ltd, Beijing 101407, China

KEYWORDS:  $\text{Co}_3\text{O}_4$ ; Metal-organic frameworks; Catalysts; Effective diffusion; Ethanol detection

## Test preparation.



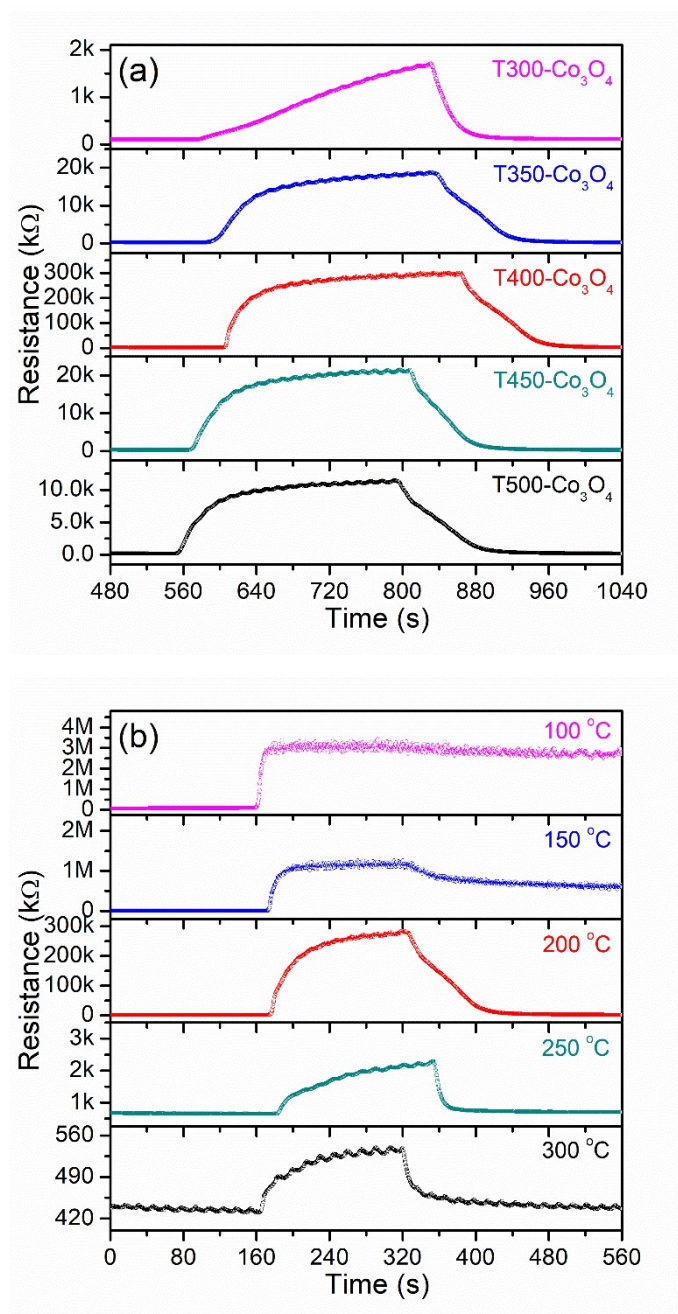
**Figure S1.** Schematic diagram for the sensing measurements.

In a typical test process, the as-prepared  $\text{Co}_3\text{O}_4$  samples (about 100 mg) were initially dispersed in absolute ethanol (about 1 mL) to form a suspension, respectively, and then dropped about  $0.2 \mu\text{L}$  suspension onto a ceramic plate substrate ( $10 \times 15 \text{ mm}$ ) using a pair of Ag electrodes. All measurements were performed in a temperature-controlled chamber into which was flowed the target gas using  $\text{N}_2$  as the carrier gas. The prepared substrate was dried at  $60 \text{ }^\circ\text{C}$  for 1 h and then transferred to the test chamber. The chamber was heated by a heating platform surrounded by a pair of probes. The resistance of each sample was acquired by the probes during testing.

The response of the samples to ethanol was calculated using Equations (1):

$$\text{Response} = R_g/R_0 \times 100\% \quad (1)$$

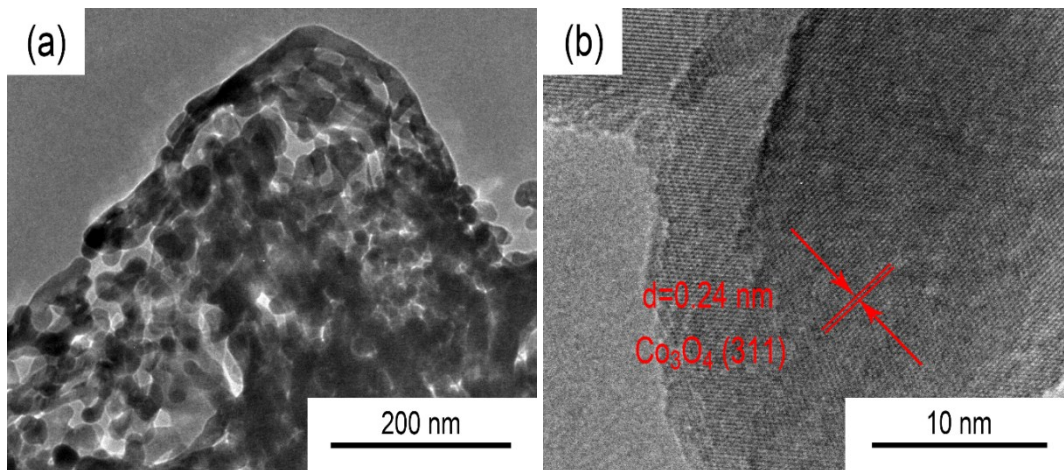
Here,  $R_g$  and  $R_0$  are the resistances of the sample in the target gas and air, respectively. In addition, the response time (i.e., time taken for the sample resistance to reach 90% of the final resistance) and recovery time (i.e., time taken for the sample resistance to return to 10% of the saturation resistance) were also determined.



**Figure S2.** Resistance dynamic curves of (a) Co<sub>3</sub>O<sub>4</sub> to 100 ppm ethanol at 200 °C, and (b) T400-Co<sub>3</sub>O<sub>4</sub> to 100 ppm ethanol with different operating temperature.

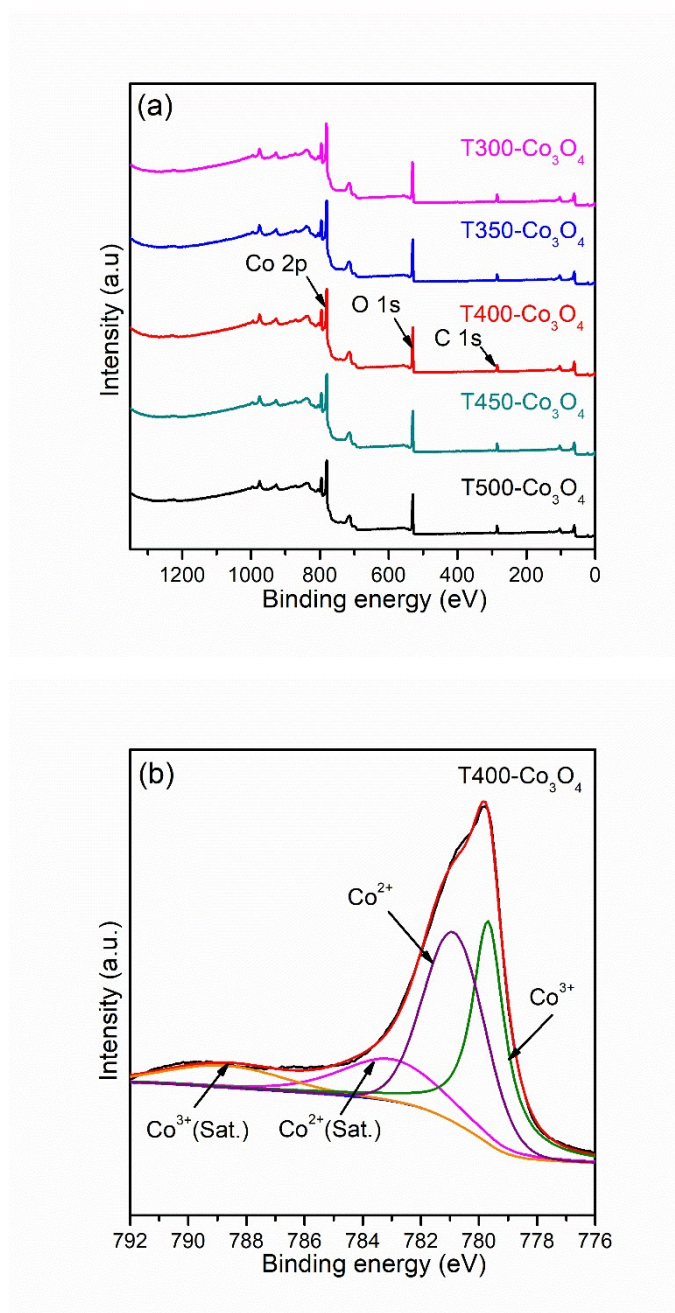
Figure S2a is the resistance dynamic curve of Co<sub>3</sub>O<sub>4</sub> to 100 ppm ethanol at 200 °C. It is clearly that the resistance of Co<sub>3</sub>O<sub>4</sub> firstly increases and followed decreases with the increase of calcination temperature. The T400-Co<sub>3</sub>O<sub>4</sub> shows the higher resistance than other samples (Figure S2a). Figure S2b is the resistance dynamic curve of T400-Co<sub>3</sub>O<sub>4</sub> to 100 ppm ethanol

with different operating temperature. Obviously, the resistance decreases with the increasing of operating temperature.



**Figure S3.** (a) TEM and (b) HRTEM images of T400-Co<sub>3</sub>O<sub>4</sub>.

Figure S3 shows TEM and HRTEM image of T400-Co<sub>3</sub>O<sub>4</sub>. Obviously, the basic unit, that is nanorods, gathered and formed rule boundary (Figure S3a). The HRTEM shows the lattice fringes information of the compound, which index to Co<sub>3</sub>O<sub>4</sub> (Figure S3b).



**Figure S4.** (a) XPS survey spectra of Co<sub>3</sub>O<sub>4</sub> samples, and (b) high resolution Co 2p XPS spectrum of T400-Co<sub>3</sub>O<sub>4</sub>.

The full range spectrum of Co<sub>3</sub>O<sub>4</sub> samples are shown in Figure S4. The sharp peaks at 780.08, 530.08 and 285.08 eV are corresponding to Co 2p, O 1s and C 1s, respectively, indicating the purity of these Co<sub>3</sub>O<sub>4</sub> samples (Figure S4a). Figure S4b is the high-resolution Co 2p XPS spectrum of T400-Co<sub>3</sub>O<sub>4</sub>. The peaks at 779.65 and 780.7 eV are corresponding to the

characteristic peak of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$ , while the satellite peak of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  are at 784.2 and 789.1 eV [1, 2].

**Table S1.** Amount (at. %) of Oxygen with different valence states in Co<sub>3</sub>O<sub>4</sub> samples.

| Sample                              | Oxygen | Surface Lattice<br>Oxygen | Oxygen<br>Vacancies | Adsorbed<br>Oxygen |
|-------------------------------------|--------|---------------------------|---------------------|--------------------|
| T300-Co <sub>3</sub> O <sub>4</sub> | 50.38  | 49.42                     | 36.88               | 13.70              |
| T350-Co <sub>3</sub> O <sub>4</sub> | 51.54  | 69.02                     | 19.25               | 11.73              |
| T400-Co <sub>3</sub> O <sub>4</sub> | 50.43  | 69.55                     | 20.88               | 9.57               |
| T450-Co <sub>3</sub> O <sub>4</sub> | 50.23  | 60.02                     | 32.55               | 7.43               |
| T500-Co <sub>3</sub> O <sub>4</sub> | 50.46  | 68.82                     | 22.31               | 8.87               |



## REFERENCES

- (S1) B. Chen, X. He, F. Yin, H. Wang, D. J. Liu, R. Shi, J. Chen and H. Yin, *Adv. Funct. Mater.*, 2017, 27, 1700795.
- (S2) X. Yi, X. He, F. Yin, B. Chen, G. Li and H. Yin, *Electrochim. Acta*, 2019, 295, 966-977.