Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supplementary Information (ESI)

## Fabrication of porous $Co_3O_4$ nanowires with high CO sensing performance at low operating temperature

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### Experimental Section

**Materials Synthesis.** The porous tricobalt tetraoxide nanowires were fabricated by the route of the solution phase and precursor. All the reagents used were AR grade and were not purified further. DI water was used throughout the experiment. Firstly, cobalt nitrate hexahydrate (25 mM) and sodium fluoride (25 mM) were dissolved in water (50 mL), and then 25 mL urea aqueous solution (50 mM) was added in the above mixed solution under stirring to obtain pink precursor solution. The as-prepared mixed solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and kept at 150 $^oC$ for 2 h after sealed. The light pink flocculent precipitates were collected by centrifugation and dried at 80 $^oC$ oven for 12 h after rinsing several times with water. The gray-black final products were produced by heating as-prepared light pink flocculent precipitates in air at 350~550 $^oC$ for 2h with a ramping rate of 2 $^oC$/min.

**Fluoride ion modification.** Commercial tricobalt tetraoxide (400 mg) and sodium fluoride (200 mg) were dissolved in water (80 mL) with stirring for 30 min to obtain black dispersion solution. Then, the above solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 150 $^{o}$C for 2 h after sealed. The black precipitates were collected by centrifugation and dried at 80 $^{o}$C oven for 12 h after rinsing several times with water. The black fluoride anion-modified tricobalt tetraoxide (denoted as F-$Co_3O_4$) powder could be obtained by heating as-prepared black precipitates in air at 350 $^{o}$C for 2h with a ramping rate of 2$^{o}$C/min. Control experiment no adding sodium fluoride was conducted under the same conditions (corresponding product denoted as C-$Co_3O_4$)

**Materials Characterizations.** The morphologies and microstructures of the products were examined by a field-emission scanning electron microscope (FESEM; JEOL, JSM-6700F, operated at 10 kV) and a high-resolution transmission electron microscope (HRTEM; JEOL, JEM-2100, 200 kV, with electron diffraction). The crystal structure and phase of the as-prepared products were characterized with X-ray powder diffraction (XRD; SHIMADZU7000, filtered Cu Kα radiation λ=0.1542 nm, at 40 kV and 100 mA). The surface element analysis of the products was performed by using X-ray photoelectron spectroscopy. (XPS; VG, ESCA LAB 220I-XL, Al Kα excitation source, voltage 9 kV, current 18.5 mA, vacuum level $10^{-7}$~$10^{-8}$ Torr). Raman spectra were collected on a Thermo Scientific Raman Microscope DXR with 532 nm laser excitation at room temperature and taken with a 50× microscope objective at 2 mW laser power on the sample. The nitrogen adsorption and desorption isotherms were measured on a Quantachrome Autosorb AS-1 instrument at 77 K with the samples outgassed at 200 °C with 2 h under vacuum before measurements. Thermogravimetry analysis (TGA) was carried out on samples placed in corundum crucibles with a heating rate of 10 K/min (TA Q600 apparatus, USA).

**Gas Sensing Measurements.** The gas-sensing experiments were performed on a homemade computer-controlled sensing test system. Firstly, The as-prepared porous $Co_3O_4$ nanowires were dropped on a UST sensor device after dispersing in water by ultrasonication and naturally dried over 12 hours. Then, the as-prepared UST sensor device would be put into gas-sensing test system for gas-sensing performance test.

The sensing operating temperature controlled by online heating resistance ranged from room temperature to 225 °C, and carbon monoxide, hydrogen and methane were tested, respectively. The gas flow concentration was controlled using a computer-controlled digital mass flow controller.

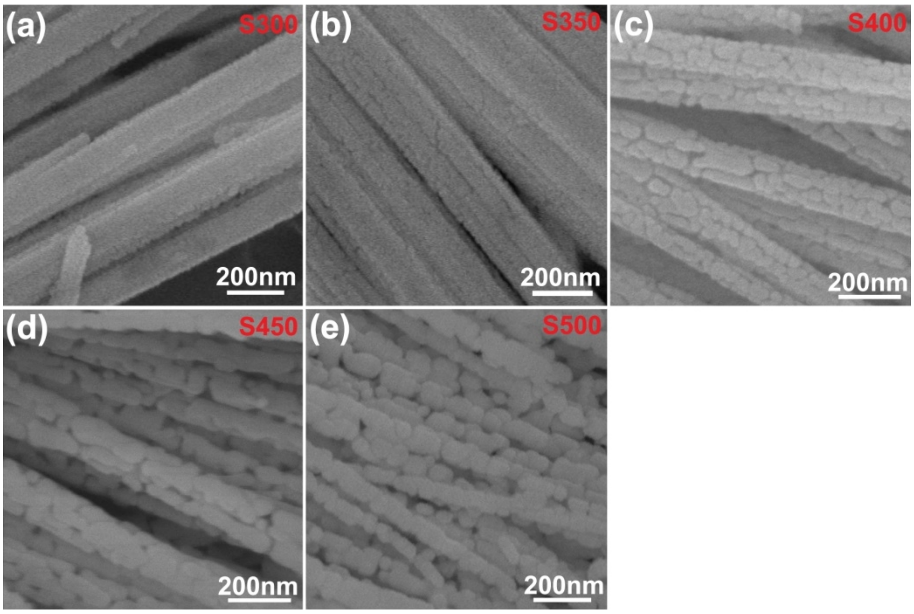

**Fig. S1** (a~e) SEM images of the products calcined at different annealing temperature.

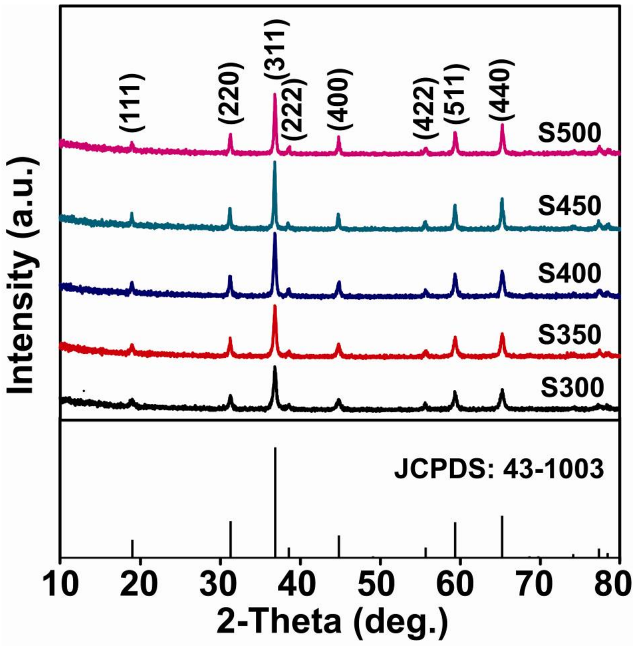

**Fig. S2** XRD patterns of S300~S500 and the reference data of JCPDS 43-1003.

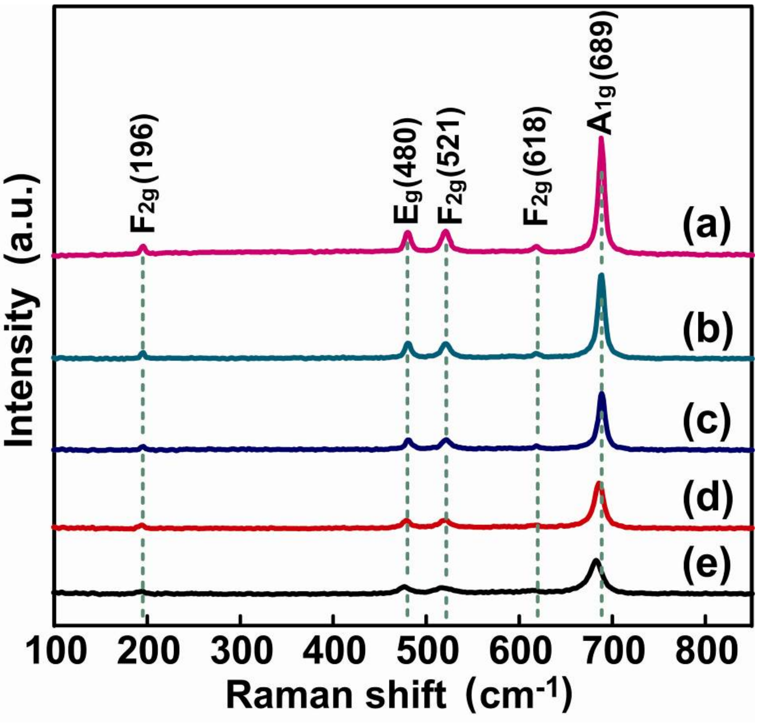

**Fig. S3** Raman spectra of (a) S500, (b) S450, (c) S400, (d) S350 and (e) S300.

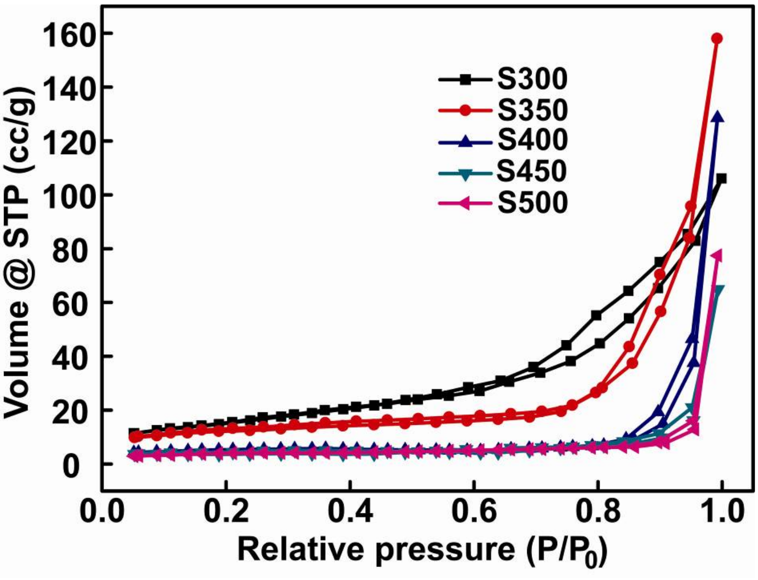

**Fig. S4** Nitrogen adsorption and desorption isotherms of the porous $Co_3O_4$ nanowires.

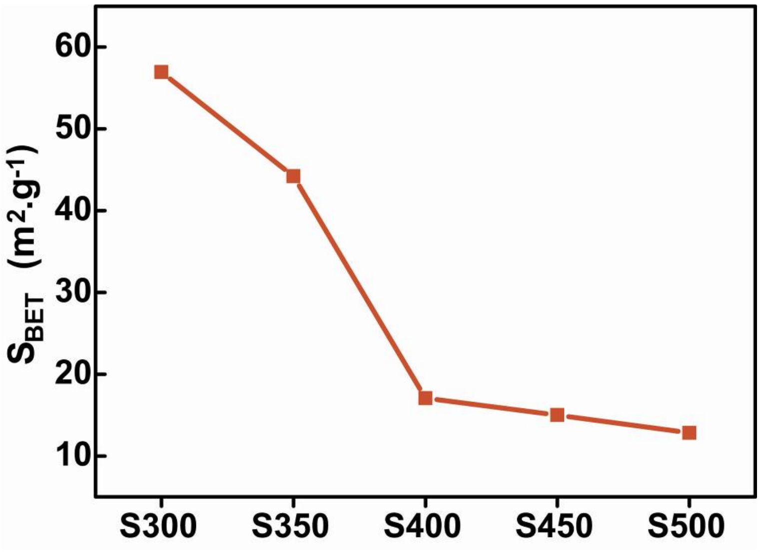

**Fig. S5** Specific surface areas of the porous $Co_3O_4$ nanowires calculated on BET method.

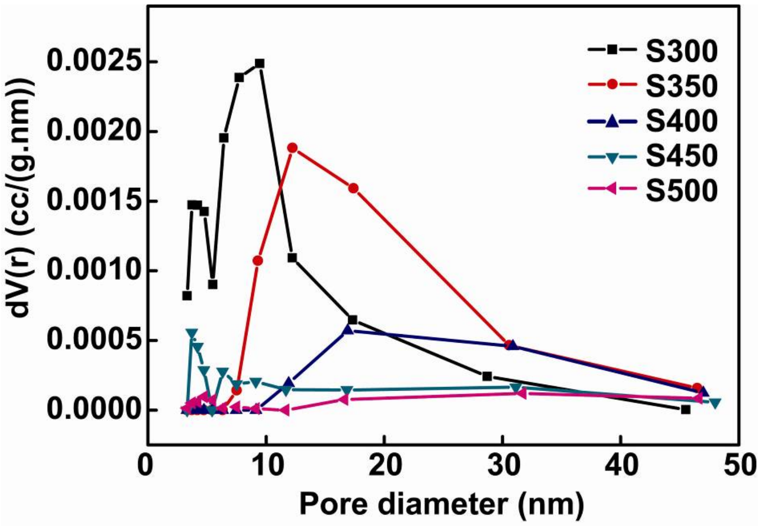

**Fig. S6** Pore diameter distribution curves of the porous $Co_3O_4$ nanowires.

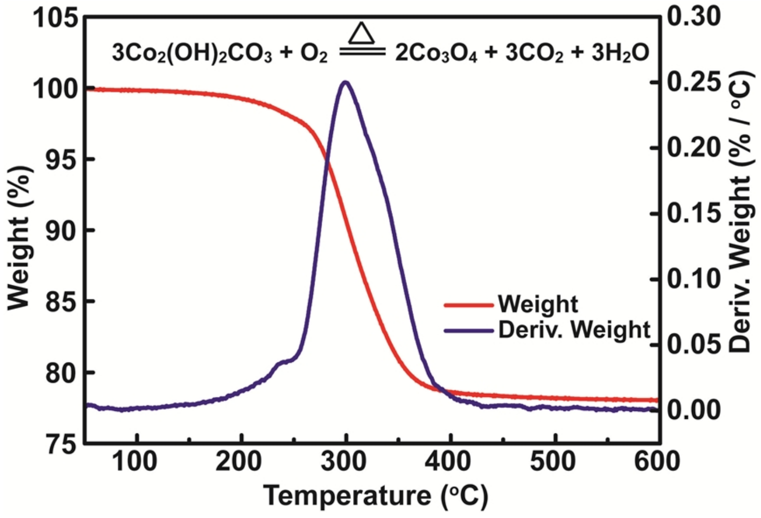

**Fig. S7** TG and DTG curves of the as-prepared cobalt carbonate hydroxide hydrate.

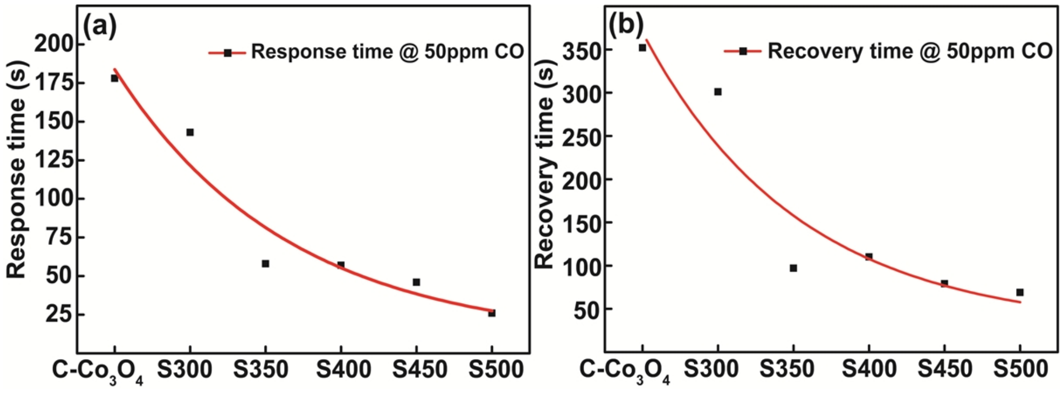

**Fig. S8** (a) Response times ($\tau_{res}$) of the different nanowires; (b) Recovery times ($\tau_{rec}$) of the different nanowires.

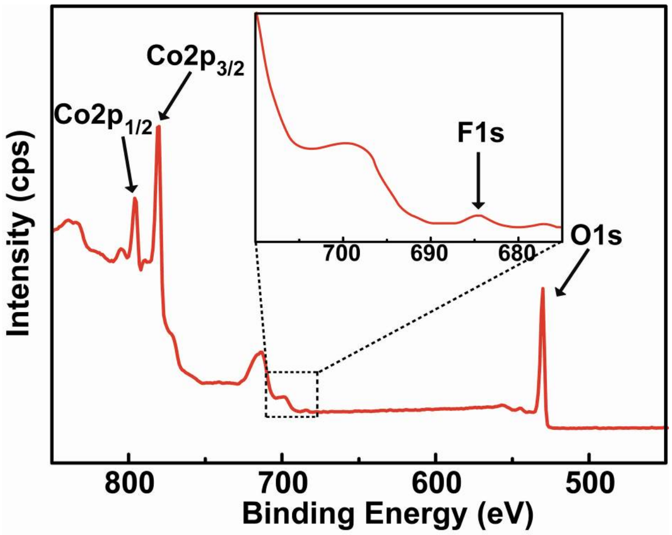

**Fig. S9** XPS spectrum of as-prepared porous $Co_3O_4$ nanowires.

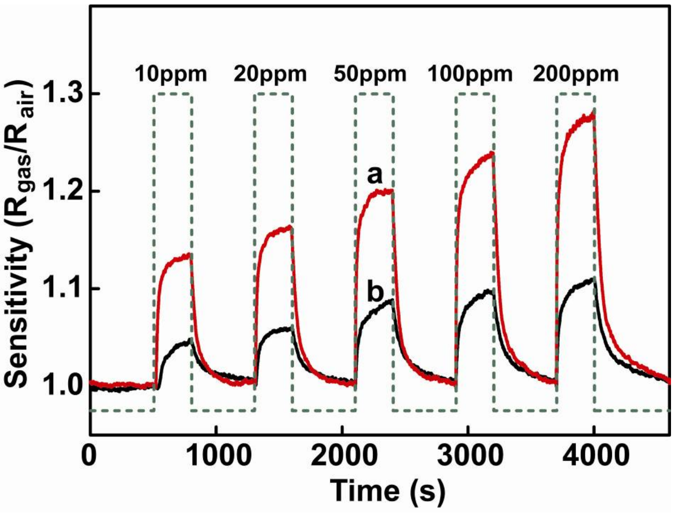

**Fig. S10** Real-time CO sensing characterization based on F-$Co_3O_4$ (a) and C-$Co_3O_4$ (b) at 100 °C operating temperature.

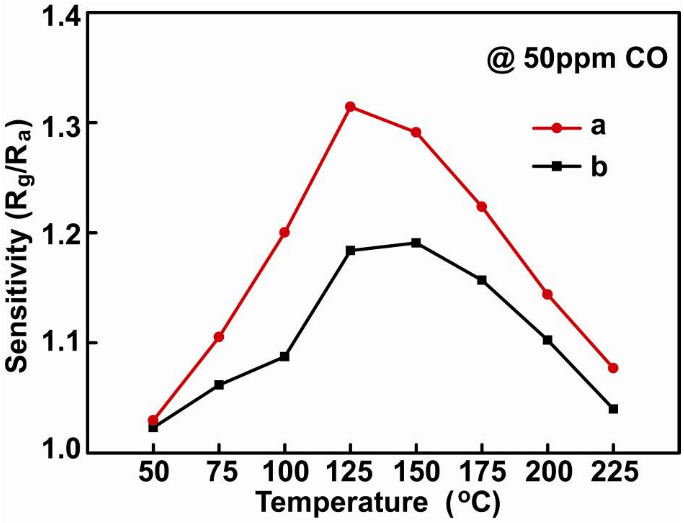

**Fig. S11** Sensitivities toward different operating temperature on F-$Co_3O_4$ (a) and C-$Co_3O_4$ (b).

**Table. S1** Optimal operating temperature of $Co_3O_4$-based gas-sensing materials in the literatures

| **Gas-sensing Materials** | **Response Gas** | **Optimal Operating Temperature** |
|---|---|---|
| **porous $Co_3O_4$ nanowires (this work)** | **CO** | **100 °C** |
| peanut-like $Co_3O_4$[1] | CO | 300 °C |
| $Co_3O_4$ nanosheets/nanorods/nanocubes[2] | $C_2H_5OH$, CO, $H_2$ | 300 ~ 400 °C |
| Au/ $Co_3O_4$[3] | $CH_4$, CO, $H_2$ | 300 ~ 330 °C |
| $Co_3O_4$ thin films[4] | CO, $H_2$ | 240 °C |
| comb-like $Co_3O_4$[5] | CO | 180 °C |
| $Co_3O_4$ nanorods[6] | CO | 250 °C |

Reference:

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