Design and construction of Co_3O_4/PEI-CNTs composite exhibiting fast responding CO sensor at room temperature

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Table S1 Summary of preparation conditions for the different samples

Sample name	Synthesis conditions
PEI-CNT	The functionalized CNTs composite with PEI.
C-24	After the precursor was placed for 24 h at room temperature, the precipitate filtrated was not washed by neither ethanol nor deionized water.
C-180	The precursor was placed for 24 h at room temperature, the precipitate was washed by ethanol and deionized water respectively, hydrothermal synthesis at 180 °C for 4 h.
C-190	The treatment conditions are similar with the C-180, except hydrothermal synthesis at 190°C.
C-200	The treatment conditions are similar with the C-180 and C-190 samples, but hydrothermal synthesis at 200°C.
C-PEI	The synthesis conditions are similar with C-190 sample, but without CNTs
C-PEI-24	After the precursor (without adding CNTs) was placed for 24 h at room temperature, the precipitate filtrated was washed by ethanol and deionized water.

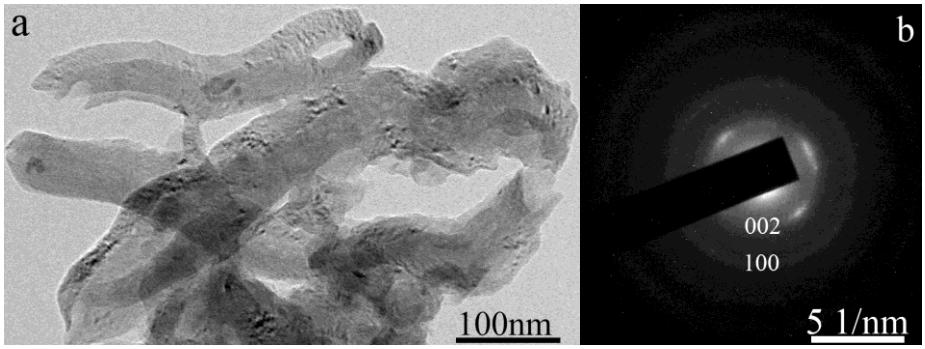

Fig.S1 TEM image (a) and SAED pattern (b) of PEI-CNTs

According to Fig.S1, the walls of the nanotubes were eroded during oxidation, which corresponded with Fig.1 and based on preferential oxidation at defect sites and breaking of nanotubes. Though the wall structures of the CNTs were eroded in oxidation in 5 h, however, the remaining parts retained good graphite structures.

Table S2 The recognitions of in situ released gas at the temperatures of max weight loss

Gases	Assigned wave number (cm^{-1})
Water vapor (H_2O)	4000-3363, 2118-1242
Carbon dioxide (CO_2)	2363, 2320, 667
Carbon monoxide (CO)	2180, 2105
Dinitrogen momoxide (NH_3)	800-1200

According to the literature,[1] the onset of a significant mass loss is at about 250 °C, while the peak concentrates at about 310 °C, corresponding to the thermal decomposition of PEI, and the raw CNTs showed a decomposition temperature of 628 °C under N_2 atmosphere, and the highest decomposition rate occurred at 740 °C. [1]

In order to evaluate the relationship between released gas in situ and weight losses, the FT-IR spectra of in-situ released gas at the maximal weigh-loss temperatures of C-190 is illustrated in Table S2.

1 W. Yan, J. Tang, Z. J. Bian, J. Hu, and H. L. Liu.,*Ind. Eng. Chem. Res.*,2012, **51**, 3653.

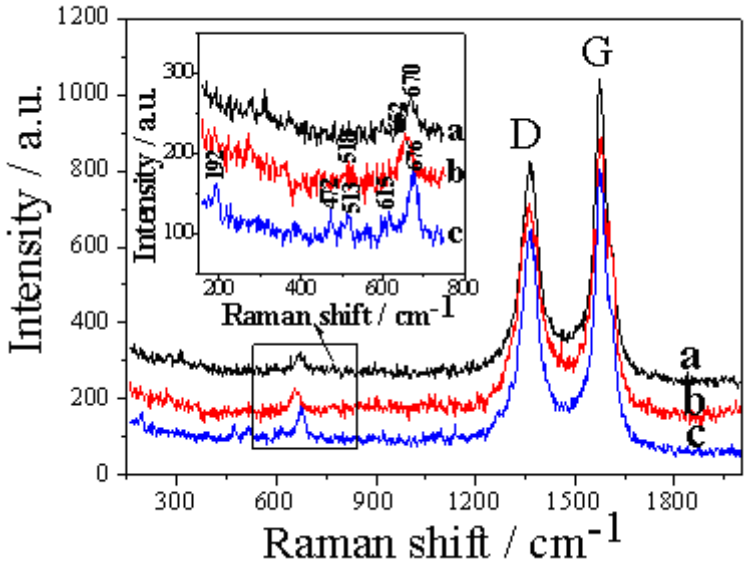

Fig .S2 Raman spectrum of the Co_3O_4/PEI-CNTs composite synthesized by different temperature (a) C-180,(b) C-190, (c) C-200 (The inset is enlarge curve of C-180,C-190 and C-200).

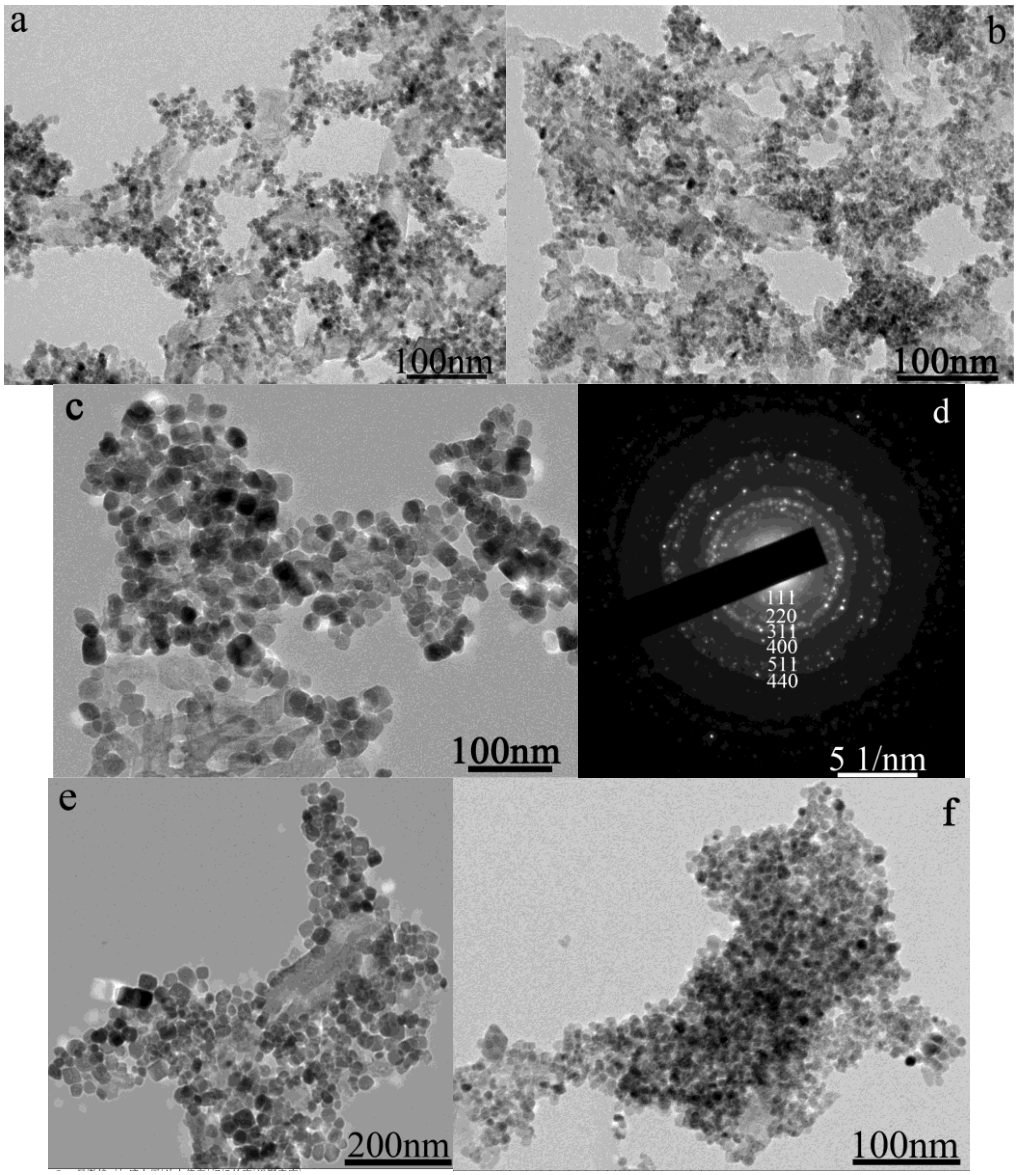

Fig.S3 TEM/HRTEM images of the Co_3O_4/PEI-CNTs and PEI-Co_3O_4 composite (a), (b) low magnification TEM images of C-180 and C-190; (c), (d), (e)TEM images of C-200 and selected area electron diffraction (SAED) pattern; (f) low magnification TEM image of C-PEI (PEI-Co_3O_4 composite).

TEM images illustrated and visually confirmed the differences between C-180, C-190, C-200 and PEI-Co_3O_4 composite. The C-200 is consisted of the aggregated nanoparticles and CNTs, or CNTs wrapped by the aggregated nanoparticle and formed the agglomerates; and the PEI-Co_3O_4 composite is mainly composed of nanoparticles and formed agglomerates.

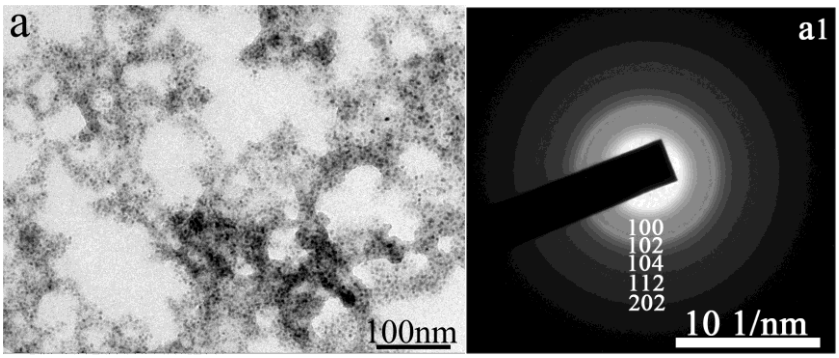

Fig . S4 TEM image (a) and SAED pattern (a1) of CoOOH/CNTs composite (C-24 sample)

After the precursor (without adding CNTs) was placed for 24 h at room temperature, the precipitate filtrated was washed by ethanol and deionized water, but no hydrothermal synthesis. The C-24 sample was obtained.

The TEM study reveals that, the nanoparticles are uniformly dispersed on the external surface of the C-24 sample, CNTs were contained in a polymer matrix, and the morphology displays the network structure (Fig. S4 (a)). Obviously, through intermolecular and intramolecular interactions, the C-24 was prepared in two-dimensional (2D) surface by self-assembly. Here, maybe the PEI and nanoparticles layer wrapping the CNTs is the main reason, or CNTs warpped by excess PEI display unclearly in Fig. S3 (a), because the precipitate filtrated was not washed by neither ethanol nor deionized water.

Fig . S4 (a1) is the SAED pattern of the C-24 sample, it displays the existence of the (100), (102), (104), (112) and (202) planes of CoOOH, respectively. It indicates that the CoOOH nanocrystalline grains were formed in the precursor at the initial stage of the reactions.

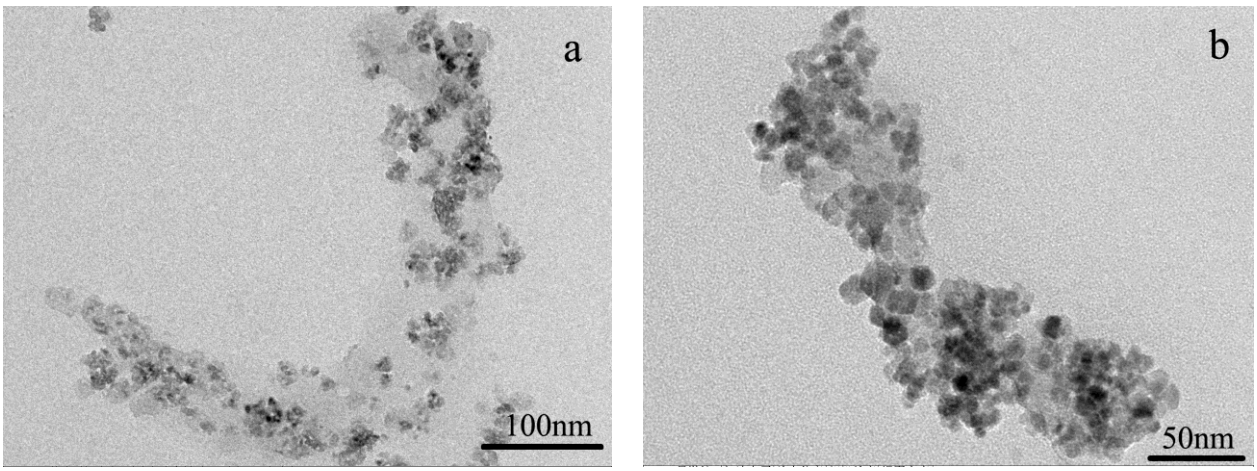

Fig. S5 TEM images of Co_3O_4/PEI-CNTs composites (C-190).

Table S3 TG results of synthesized samples

Samples	(TG under N_2) ΔW_{PEI}%	(TG under air) $\Delta W_{Co_3O_4}$%
C-200	(135~400 °C) 8.16	(After 500 °C) 49.7
C-190	(200~400 °C) 9.12	(After 560 °C) 41.7
C-180	(135~380 °C) 9.73	(After 500 °C) 22.1

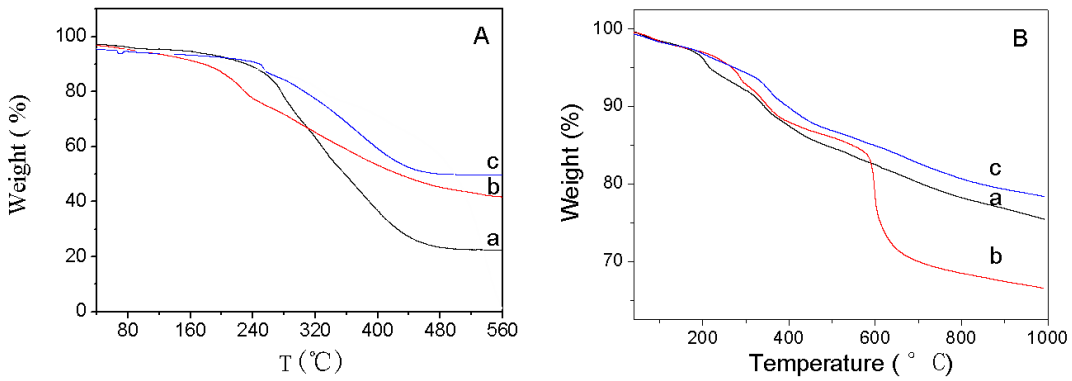

Fig.S6 TG curves of the samples synthesized by hydrothermal method at different temperature with a temperature ramp of 8 °C/min under air (A) and N_2 (B).
(a) C-180; (b) C-190; (c) C-200

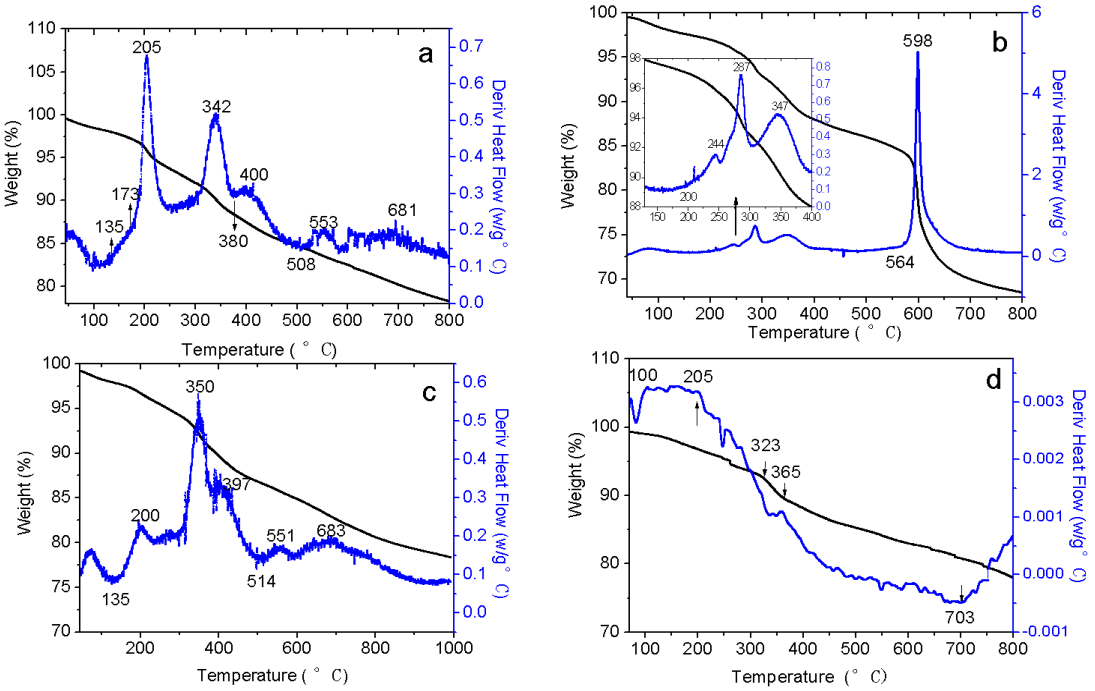

Fig.S7 TG-DTA curves of the samples synthesized by hydrothermal method at different temperature with a temperature ramp of 8 °C/min under pure N_2
(a) C-180, (b) C-190, (c) C-200, (d) PEI-CNTs

The TG-DTA curves of the Co_3O_4/CNTs composites are illustrated in Fig.S7. The PEI content of the Co_3O_4/CNTs composites are calculated with 135-400 ^oC temperatures range. The results are list in Table S3. Fig.S7 shows the TG-DTA results of PEI-CNTs and the Co_3O_4/PEI-CNTs composite under N_2.

As shown in Fig.S7a, there are five exothermic peaks/oxidation peaks in C-180, the started temperatures of oxidation are 135 ^oC from room temperature to 400 ^oC, and the started temperatures of oxidation are 508 ^oC from 400 to 800 ^oC. For C-190 and C-200, they have four or fine exothermic peaks/oxidation peaks, respectively. The started temperatures of oxidation are 200 and 135 ^oC from room temperature to 400 ^oC, the started temperatures of oxidation are 564 and 514 ^oC from 400 to 800 ^oC (see Fig .S7 (b, c)).

It is to known, the exothermic peaks/oxidation peaks before 400 ^oC are due to the dissociation and oxidation of PEI [1] in comparison with the PEI-CNTs sample (see Fig.S7(d)). And the exothermic peaks/oxidation peaks between 500 and 800°C are due to the dissociation and oxidation of CNTs (see Fig.S7) [1]. The samples was performed under N_2, therefore, Co_3O_4 can be regarded as an oxygen reservoir. Fig.S7 (d) shows that, there is no exothermic peaks/oxidation peaks in PEI-CNTs sample because of without Co_3O_4.

Table S4 BET results of the synthesized samples

Sample	BET specific surface /cm^{-2}	Pore size /nm
C-200	96.5	7.6
C-190	114.1	12
C-180	111	9.7

The C-200 shown in Fig. 4(d) and Fig. S3(c, e) revealed well-crystallized Co_3O_4 particles with a wide size distribution (about 10-30 nm, see the inset of diameter distribution of C-200 in Fig. 4d), and highly agglomerated. Therefore the C-200 BET specific surface is smaller.

Fig. 4(a, b) show the TEM images for the prepared C-180, in which the sample (Fig. 4a) appears to possess the loosely packed structure, with the C - 190 is very similar, so the C-180 and C-190 is similar to the specific surface area. But, the crystallinity of the C-180 is not enough.

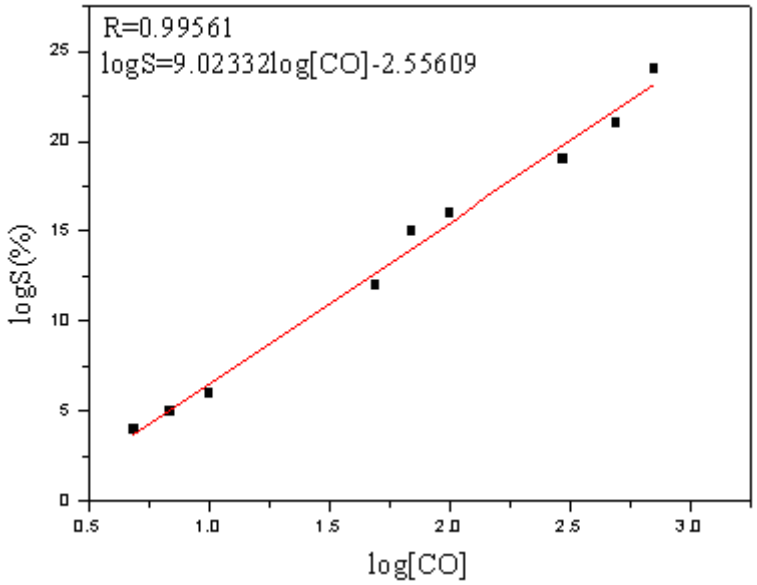

Fig.S8CO calibration curve of the Co_3O_4/PEI-CNTs composite (C-190) sensor from 700 ppm to 5 ppm.

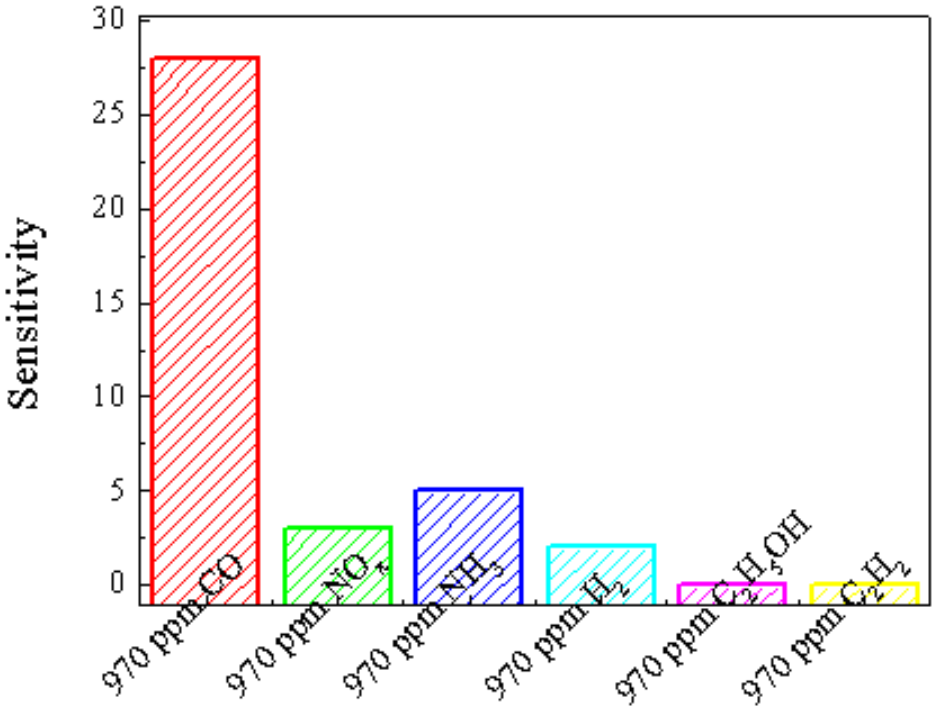

Fig.S9 The selectivity of Co_3O_4/PEI-CNTs composite (C-190) at room temperature.

Table S5 The results of thin film gas sensors at room temperature in air

Sample	CO ppm (700) /sensitivity (%)	CO ppm (500) /sensitivity (%)	CO ppm (300) /sensitivity (%)	CO ppm (5) /sensitivity (%)
C-200	12	9	7	-
C-190	24	21	18	4
C-180	6	5	5	-
C-PEI-24	3	-	-	-
C-PEI	2	-	-	-
CNTs	-	-	-	-

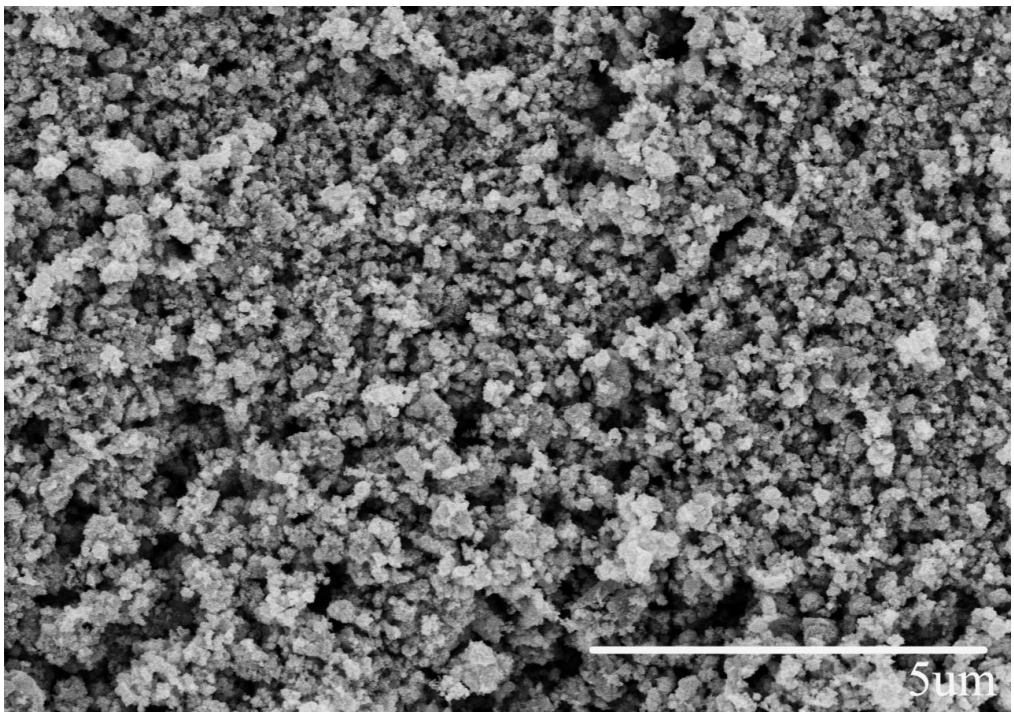

Fig.S10 SEM image of the Co_3O_4/PEI-CNTs composite gas sensor film

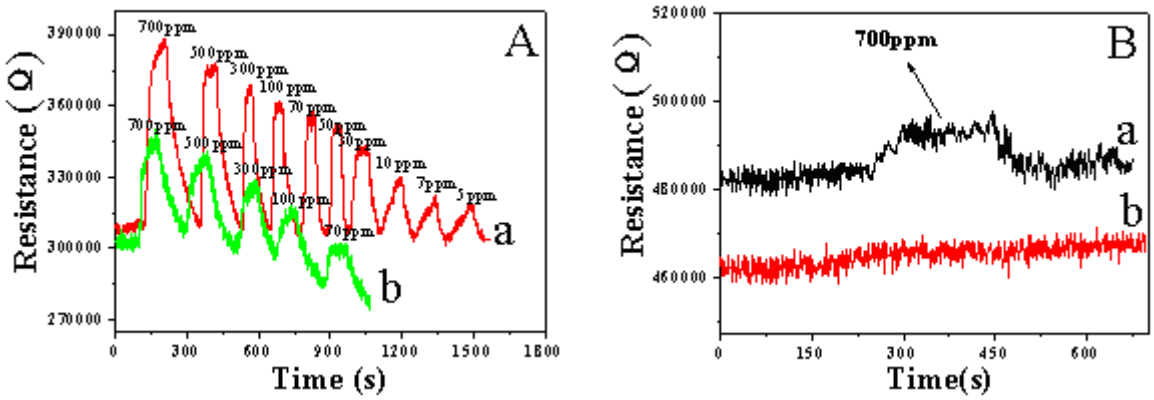

Fig . S11 Dynamic response-recovery curves of the A (a, Co_3O_4/PEI-CNTs composite, b, Co_3O_4 nanocrystals) and B (a, PEI-CNTs composite, b, the functionalized CNTs) thin film sensor to 5-700 ppm CO at room temperature in air (humidity 26%).