

Electronic Supplementary Information

**Stably dispersed carbon nanotubes covalently bonded with  
phthalocyanine cobalt(II) for ppb-level H<sub>2</sub>S sensing at room  
temperature**

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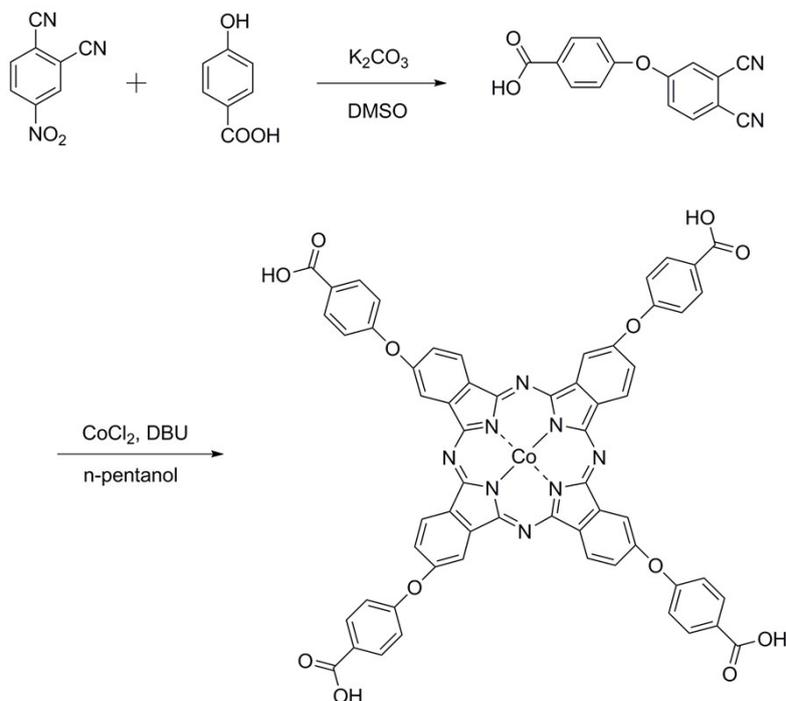
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## Experiment details

### 1.1. Materials

All chemicals and solvents in this work were of analytical grade and were used as-received. The synthetic scheme of tetra- $\beta$ -carboxyphenoxyphthalocyanine cobalt(II) (cPcCo) is shown in Scheme S1.



**Scheme S1.** Synthetical scheme of tetra- $\beta$ -carboxyphenoxyphthalocyanine cobalt(II)

### 1.2. Instrument and methods

Elemental analyses of C, H and N were carried out on a Vario MICRO elemental analyzer. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> solutions) were recorded at 500 MHz on a Bruker Advance AV-500 instrument. EI and MALDI-TOF mass spectra were performed using an Agilent spectrometer (HP 5973N) and a Bruker microflex LT (Bruker Daltonics, Bremen, Germany) mass spectrometer, respectively. UV/Vis absorption spectra were recorded with a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, USA). FT-IR spectra were recorded on a Nicolet FT-IR NEXUS spectrometer (Thermo Scientific).

### 1.3. Preparation of aCNT

Pristine carbon nanotube (CNT, 3.0 g) was added into a solution of H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> mixture (Volume<sub>H<sub>2</sub>SO<sub>4</sub></sub>/Volume<sub>HNO<sub>3</sub></sub>=3 : 1, 98 % and 68 % purity, 120 mL) at room

temperature, and then stirred for 12 h in water bath at 50 °C. After being cooled to about 20 °C, the reaction mixture was poured slowly into ice water (500 mL) under continuous stirring. Thereafter, the black sediments were centrifuged and washed with distilled water, and then stirred in a H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> mixture (Volume H<sub>2</sub>SO<sub>4</sub>/Volume H<sub>2</sub>O<sub>2</sub>= 3 : 1, 98 % and 30 % purity, 160 mL) at 80 °C for 1 h. Finally, the resulting product was collected by centrifugation and washing with distilled water until the pH of the supernatant solution approached 7, and dried in a vacuum oven at 50 °C for 12 h.

#### 1.4. Synthesis of 4-(4-carboxyphenoxy) phthalonitrile

4-Nitrophthalonitrile (6.93 g, 0.040 mol) was dissolved in DMSO (160 mL) under a nitrogen atmosphere and p-hydroxybenzoic acid (10.97 g, 0.080 mol) was added to the solution. After stirring for 30min, anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (19.35 g, 0.14 mol) was added portion-wise over 3 d with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 5 days. Then the solution was poured into ice-water (500 mL) with stirring. The solid residue was removed by filtrating, and the filtrate was acidified by addition of concentrated hydrochloric acid to pH 1-2 with stirring, and left to stand for 10 min. The resulting precipitate was collected by filtration, washed with distilled water and then vacuum dried. The rough product was further purified by silica gel column chromatography, eluting with trichloromethane /acetone (5 : 1, V/V), eventually to form white crystals 4-(4-carboxyphenoxy) phthalonitrile. Yield: 95 %. Anal. Calcd (found) C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 68.18 (68.17); H, 3.03 (3.10); N, 10.61 (10.70). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ ppm): 7.55(s, 1H, benzene C-H), 7.95(s, 1H, benzene C-H), 8.15(s, 1H, benzene C-H), 7.25(d, 2H, benzene C-H), 8.05(d, 2H, benzene C-H), 13.05(s, 1H, hydroxyl O-H) EI-MS Calcd (Found): m/z= 264.05(264)[M<sup>+</sup>].

#### 1.5. Synthesis of tetra-β-carboxyphenoxyphthalocyanine cobalt(II) (cPcCo)

4-(4-Carboxyphenoxy)phthalonitrile (2.64 g, 0.010 mol), anhydrous cobalt (II) chloride (0.39 g, 0.003 mol) and 1,8-dicyanobicyclo-[5.4.0]-undec-7-ene (DBU) (4.0 mL) were taken into a solution of freshly distilled *n*-amyl alcohol (60 mL) at room temperature. The ensuing mixture was refluxed for 20 h with continuous stirring

under a nitrogen atmosphere. After natural cooling to about 20 °C, the precipitate was filtered, washed successively with methanol (50 mL) and acetone (50 mL), and then dissolved in a solution of potassium hydroxide (1 mol L<sup>-1</sup>, 100 mL) while stirring. The solid residue in the solution was removed by filtrating, and the filtrate was acidified by addition of concentrated hydrochloric acid to pH 3-4 with stirring, and left to stand overnight. The resulting precipitate was collected by centrifugation, washed with distilled water until the pH of the supernatant approached 7 and then dried in a vacuum oven at 50 °C to obtained purple-black crystals of cPcCo. Yield: 40.0 %. Anal. Calcd (found) C<sub>60</sub>H<sub>32</sub>N<sub>8</sub>O<sub>12</sub>Co: C, 64.57 (64.43); H, 2.87 (2.92); N, 10.04 (10.14). Electronic absorption spectrum (UV-Vis) in DMF: λ<sub>max</sub> (nm) = 664, 603. FT-IR spectra (KBr pellets) ν: 3462, 1693, 1599, 1505, 1471, 1409, 1323, 1237, 1161, 1117, 1095, 1058, 1012, 956, 879, 852, 770, 752 cm<sup>-1</sup>. MALDI-TOF -MS Calcd (Found): m/z= 1115.15(1115)[M<sup>+</sup>].

#### **1.6. Preparation of cPcCo/aCNT hybrid**

aCNT (0.10 g) was sonicated in N, N-dimethylformamide (DMF) solution (20 mL) at room temperature for 2 h, and then the corresponding cPcCo (0.20 g) in powders was added under vigorous stirring. The ensuing mixture was sonicated for further 48 h at 50 °C. After cooling, the resultant solution was filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane filter, and washed continuously by methanol, DMF and acetone until the filtrate was colorless. After that, the paste-like filter-cake was dried in a vacuum oven at 50 °C for 1 h, and finally the cPcCo/aCNT hybrid was achieved as black powders.

## Result and discussion

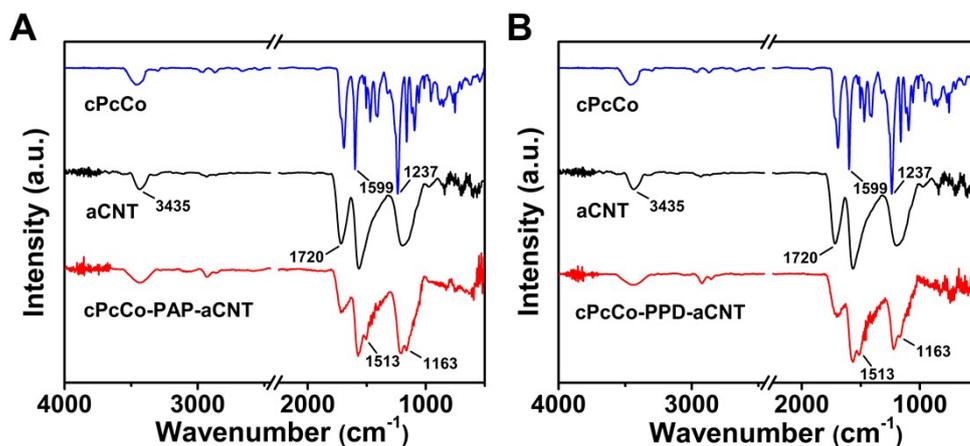


Fig. S1 (A) FT-IR spectra of cPcCo, aCNT, and cPcCo-PAP-aCNT hybrid; (B) FT-IR spectra of cPcCo, aCNT, and cPcCo-PPD-aCNT hybrid.

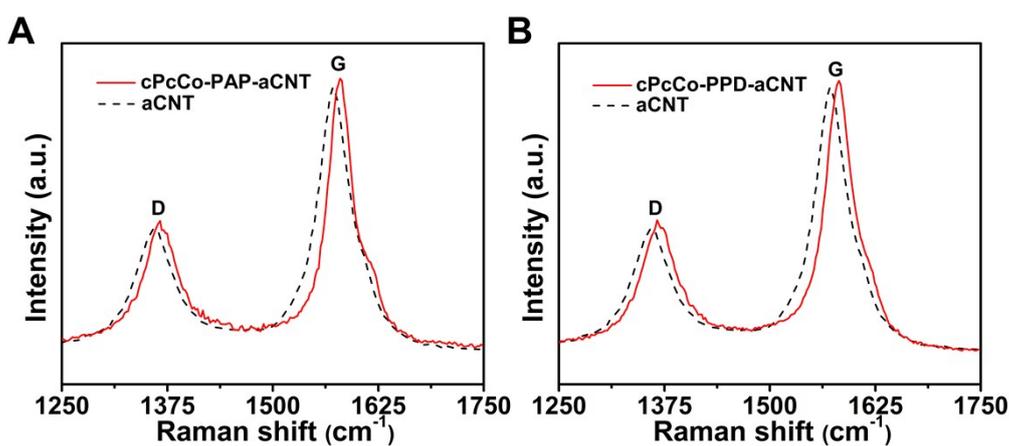


Fig. S2 (A) Raman spectra of aCNT and cPcCo-PAP-aCNT hybrid; (B) Raman spectra of aCNT and cPcCo-PPD-aCNT hybrid (obtained at  $\lambda_{exc} = 457.9$  nm).

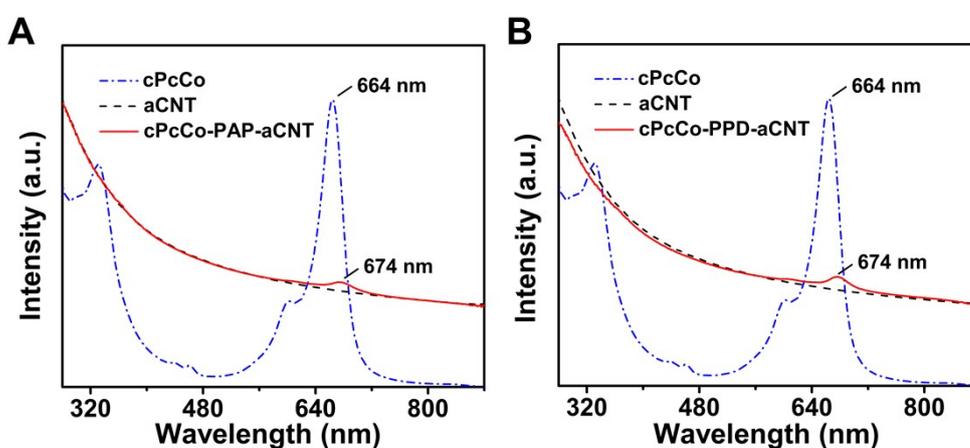
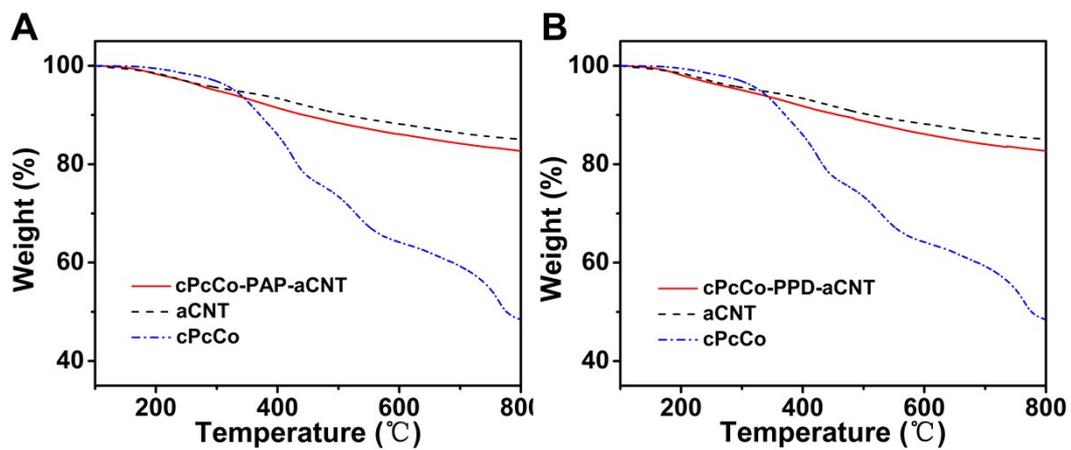
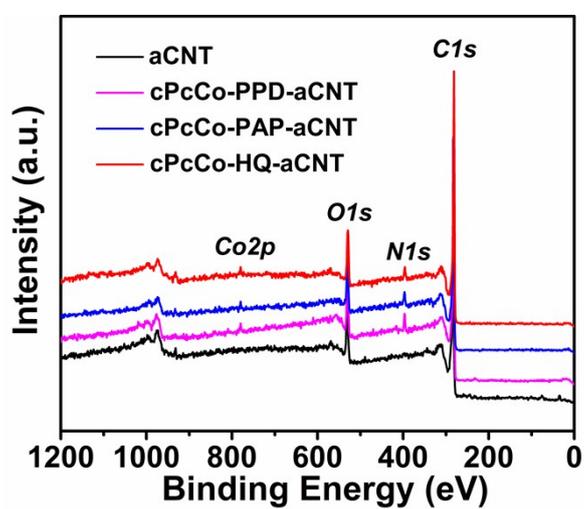


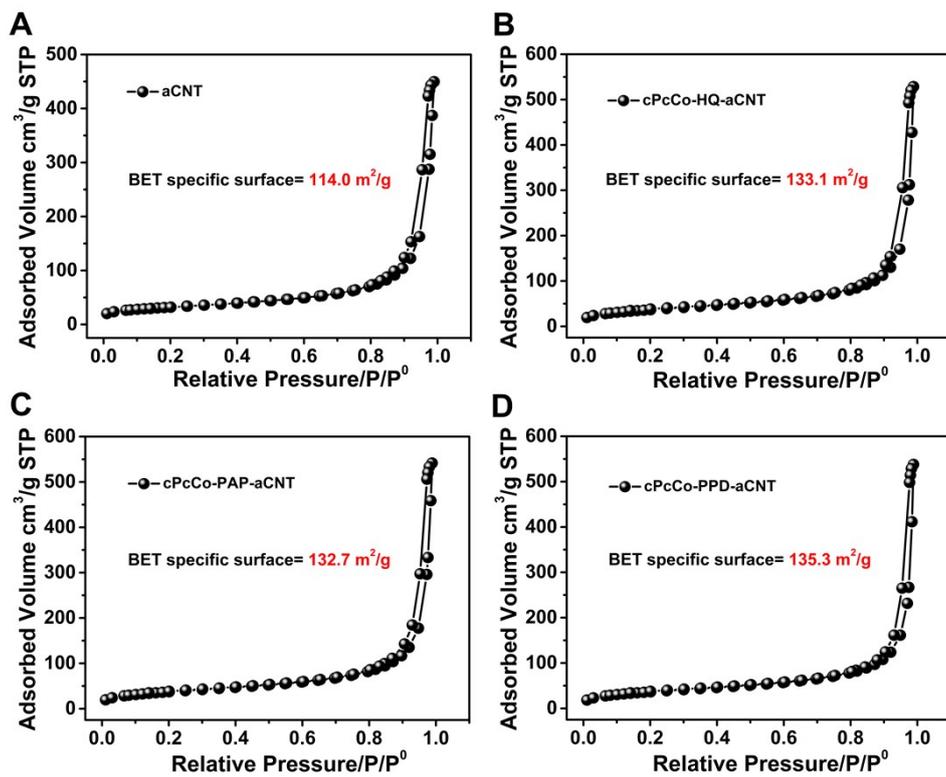
Fig. S3 (A) UV-vis spectra of cPcCo, aCNT and cPcCo-PAP-aCNT hybrid; (B) UV-vis spectra of cPcCo, aCNT and cPcCo-PPD-aCNT hybrid.



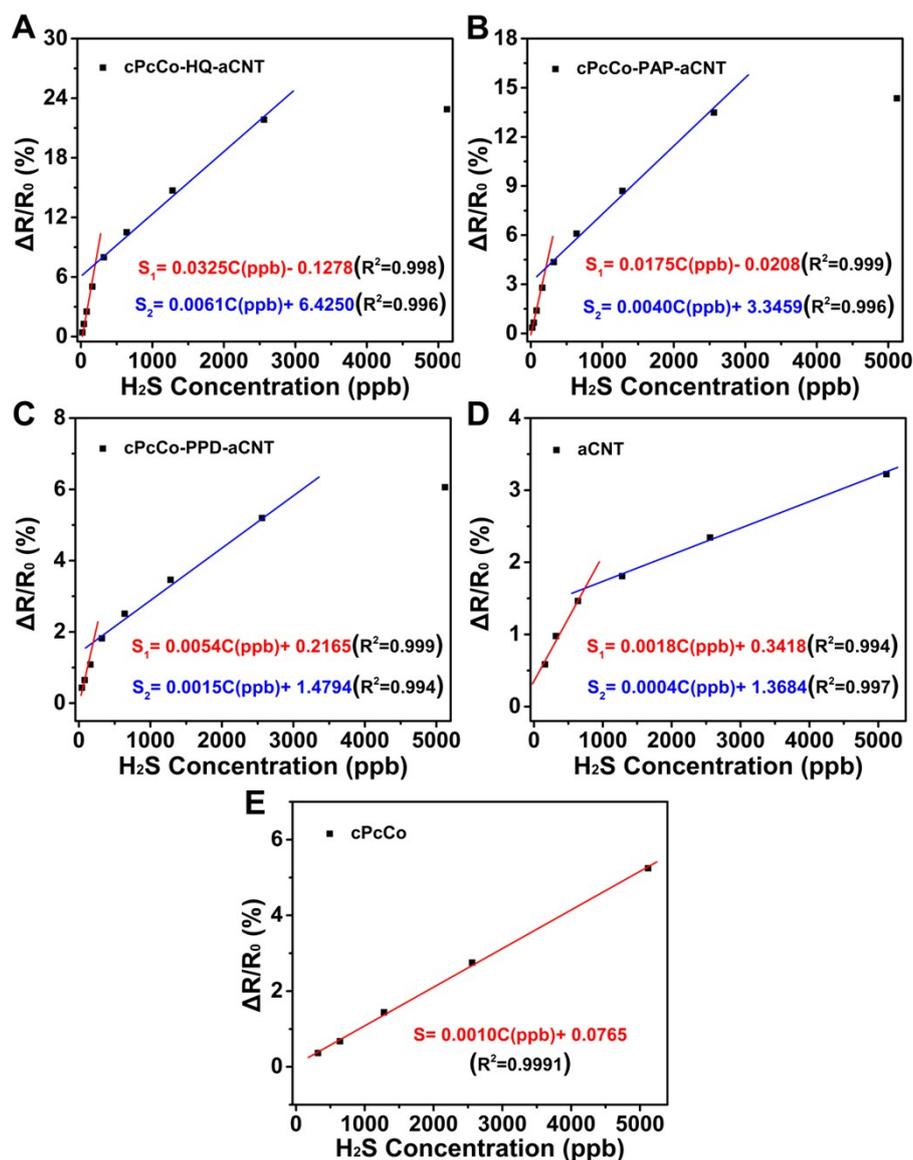
**Fig. S4** (A) TGA profiles of cPcCo, aCNT and cPcCo-PAP- aCNT hybrid; (B) TGA profiles of cPcCo, aCNT and cPcCo-PPD-aCNT hybrid.



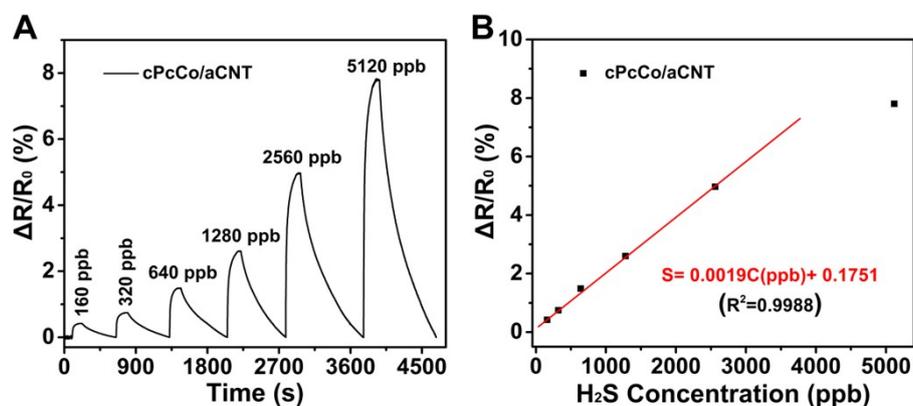
**Fig. S5** XPS survey spectrum of aCNT, cPcCo-HQ-aCNT, cPcCo-PAP-aCNT, and cPcCo-PPD-aCNT hybrid.



**Fig. S6**  $\text{N}_2$  adsorption-desorption isotherms of aCNT (A), cPcCo-HQ-aCNT (B), cPcCo-PAP-aCNT (C), and cPcCo-PPD-aCNT hybrid (D).



**Fig. S7** The calibration linear relationship of response versus the H<sub>2</sub>S concentration, (A) cPcCo-HQ-aCNT sensor, (B) cPcCo-PAP-aCNT sensor, (C) cPcCo-PPD-aCNT sensor, (D) aCNT, and (E) cPcCo.



**Fig. S8** (A) Response of cPcCo/aCNT sensor upon exposure to varying concentrations of H<sub>2</sub>S; (B) the calibration linear relationship of response versus the H<sub>2</sub>S concentration.

**Table S1.** Comparison of the detection performances of cPcCo-HQ-aCNT, cPcCo-PAP-aCNT, cPcCo-PPD-aCNT, aCNT, cPcCo and cPcCo/aCNT sensors to H<sub>2</sub>S (RH: 60 %).

Sensor material	Response (%) / Detection conc. (ppb)	Detection limit (ppb)	Response time (s) / Detection conc. (ppb)	Recovery time (s) / Detection conc. (ppb)
cPcCo-HQ-aCNT	7.98/320; 10.50/640; 14.69/1280	5	60/320; 68/640; 77/1280	598/320; 1026/640; 1086/1280
cPcCo-PAP-aCNT	4.35/320; 6.09/640; 8.70/1280	9	74/320; 81/640; 101/1280	572/320; 995/640; 1171/1280
cPcCo-PPD-aCNT	1.82/320; 2.51/640; 3.46/1280	28	93/320; 98/640; 111/1280	554/320; 1019/640; 1197/1280
aCNT	0.98/320; 1.46/640; 1.76/1280	74	43/320; 66/640; 67/1280	896/320; 1208/640; 1315/1280
cPcCo	0.36/320; 0.68/640; 1.44/1280	128	21/320; 36/640; 33/1280	121/320; 190/640; 211/1280
cPcCo/aCNT	0.74/320; 1.48/640; 2.60/1280	84	48/320; 56/640; 65/1280	430/320; 474/640; 455/1280

**Table S2.** Comparison of the detection performances of different H<sub>2</sub>S sensors

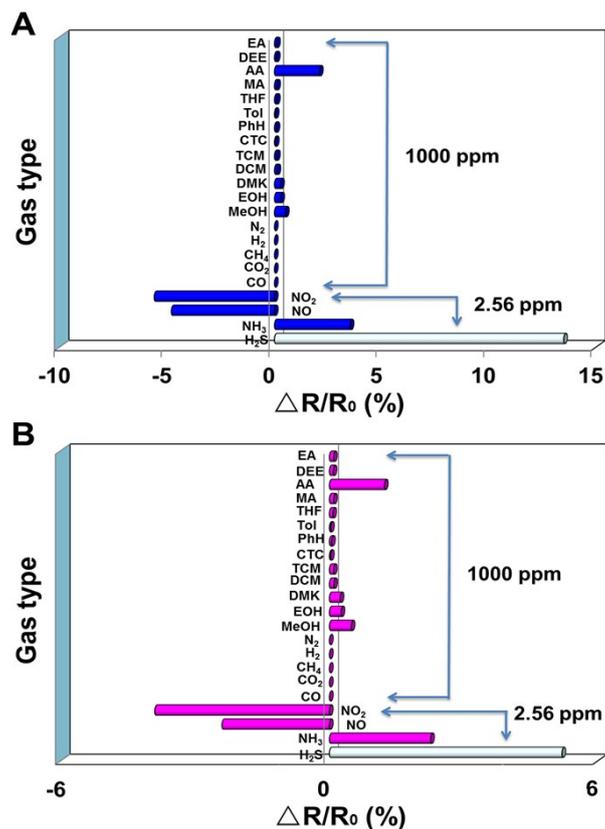
Sensor material	Response (%) / Detection conc. (ppm) <sup>[b]</sup>	Detection limit (ppm) <sup>[a]</sup>	Working temperature (°C) <sup>[c]</sup>	Response time (s) / Detection conc. (ppm) <sup>[b]</sup>	Recovery time (s) / Detection conc. (ppm) <sup>[b]</sup>	Detection range (ppm)	Ref.
carbon nanotube networks	1.4/0.05	0.05	RT	~240/0.05	~120/0.05	0.05-0.5	1
Titania Nanowires	11/80	10	140	~705/80	—	10-80	2
Cu <sub>2</sub> O/SnO <sub>2</sub> film	65.1/50	0.5	RT	160/50	240/50	0.5-50	3
α-Fe <sub>2</sub> O <sub>3</sub> nanochains	1.6/1	1	285	8.6/5	65.7/5	1-100	4
α-Fe <sub>2</sub> O <sub>3</sub> nanosphere	3.4/1	1	350	8.9/10	—	1-100	5
CuO/SnO <sub>2</sub> nanowires	15/10	0.1	300	9/10	8/10	0.1-10	6
WO <sub>3</sub> Nanofibers/ Graphene	69.3±2.5/5	0.1	300	—	—	0.1-5	7
SnO <sub>2</sub> Nanocrystals	20.4/0.5	0.5	160	—	—	0.5-30	8
Au@NiO yolk– shell nanoreactors	108.9/5	1.25	300	—	—	1.25-5	9
ZnO/ZnS core–shell	5.9/1	1	RT	70/1	100/1	1-50	10
In <sub>2</sub> O <sub>3</sub> /ZnO core –shell	92.5/700	20	RT	—	—	20-700	11
Fe <sub>2</sub> O <sub>3</sub> /graphene nanosheets	450/15	10	190	500/15	~30/15	—	12
Mo-doped ZnO nanowire	14.1/5	0.2	300	—	—	0.2-5	13
PSS-doped PANI/graphene nanocomposites	20/1	1	RT	~90/1	~150/1	1-50	14
SnO <sub>2</sub> @rGO nanostructure	78/10	2	100	7/2	—	2-10	15

Cu/ZnO nanowire	35.4/100	100	RT	100/500	60/500	100-1000	16
In <sub>2</sub> O <sub>3</sub> @WO <sub>3</sub> nanocomposites	143.4/10	0.5	150	~100/5	~390/5	0.5-10	17
Au/SnO <sub>2</sub> spheres	5.7/0.1	0.1	400	18/5		0.1-5	18
<b>cPcCo-HQ-aCNT</b>	<b>0.4/0.02; 1.3/0.04; 2.5/0.08</b>	<b>0.005</b>	<b>RT</b>	<b>30/0.08</b>	<b>520/0.08</b>	<b>0.02-5.12</b>	<b>This work</b>

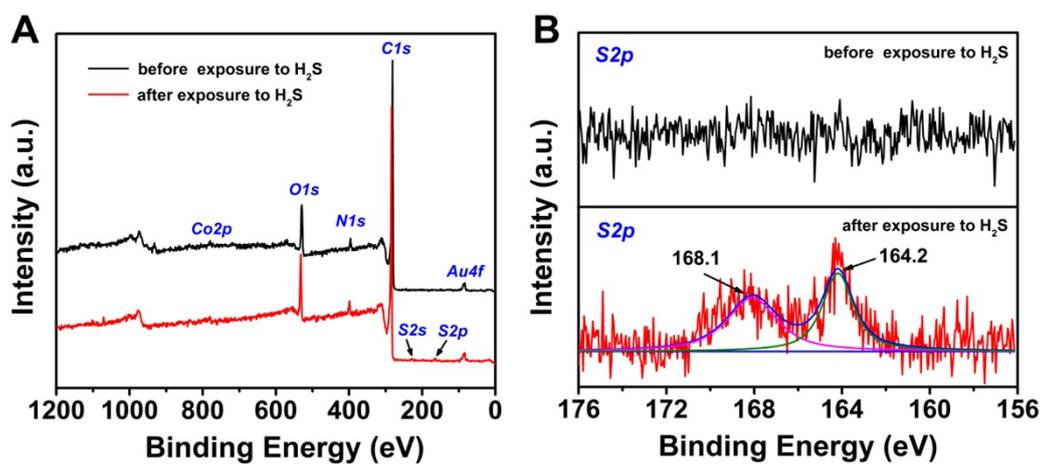
[a] If the sensor detection limit was not explicitly provided in the original report, then the lowest tested analyte concentration is listed.

[b] If the response (%), response time (s) or recovery time (s) of the sensor was not explicitly provided in the original report, then the estimate from the curve in that report is listed.

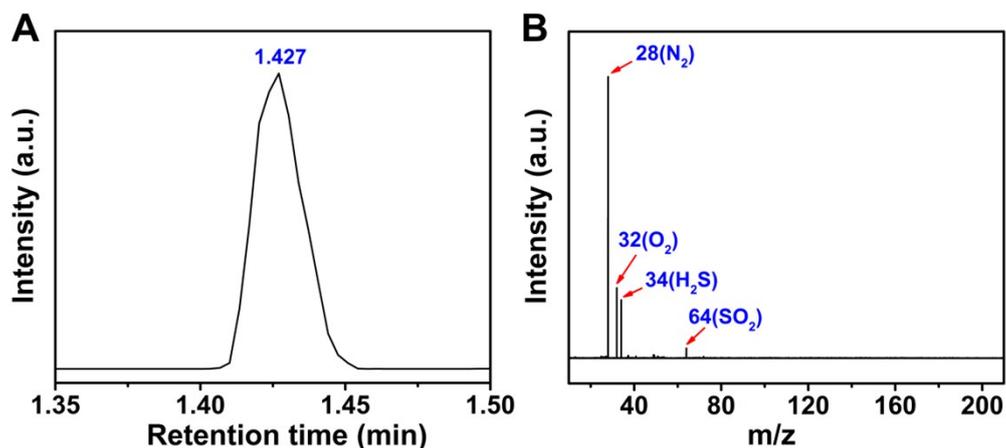
[c] RT, abbreviation for room temperature.



**Fig. S9** Cross-sensitivities to various gases for the cPcCo-PAP-aCNT sensor (A) and cPcCo-PPD-aCNT sensor (D) at room temperature; MeOH = methanol, EtOH = ethanol, DMK = acetone, DCM = dichloromethane, TCM = trichloromethane, CTC = carbon tetrachloride, PhH = benzene, Tol = toluene, THF = tetrahydrofuran, MA = Methyl Aldehyde, AA = acetic acid, DEE = diethyl ether, and EA = ethyl acetate.



**Fig. S10** (A) XPS survey spectra and (B) high-resolution S2p XPS spectra of cPcCo-HQ-aCNT sensor before and after exposure to H<sub>2</sub>S at room temperature.



**Fig. S11** (A) Gas chromatogram and (B) Mass spectrum after cPcCo-HQ-aCNT sensor exposure to H<sub>2</sub>S at room temperature.

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