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## 1. Introduction

Hydrogen sulphide ( $H_2S$ ) is a common and extremely dangerous gas, which often results from bacterial activity in anaerobic wastewater, volcanic gas, coal mines, oil and natural gas industries, and is released as a by-product in some manufacturing industries.<sup>1-6</sup> In daily life, exposure to  $H_2S$  is potentially fatal,<sup>7-9</sup> because it may stimulate the eyes and respiratory tract, cause dizziness and nausea, and even lead to suffocation, lung injury and sudden death. Therefore, it is important to develop sensors based on novel materials with high sensitivity and selectivity, low detection limit, and energy saving for monitoring  $H_2S$ . Although various metal oxides,<sup>10-15</sup> metal-doped oxides,<sup>16-18</sup> and composite materials of metal oxides<sup>19-23</sup> have been successfully developed as electrical  $H_2S$ 

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

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Cost-efficient, highly sensitive and stable sensing materials play a key role in developing H<sub>2</sub>S sensors. Herein, tetra- $\beta$ -carboxyphenyloxyphthalocyanine cobalt(II) (cPcCo) has been successfully bonded on the surface of acidified multiwalled carbon nanotubes (aCNTs) by a facile two-step condensation reaction in the presence of N,N'-dicyclohexylcarbodiimide (DCC), using hydroquinone (HQ), p-aminophenol (PAP), and p-phenylenediamine (PPD) as linking molecules, respectively. The obtained cPcCo-B-aCNT (B= HQ, PAP, and PPD) hybrids display good dispersibility in ethanol, which is beneficial to construct uniform sensing devices. The cPcCo-B-aCNT sensors, with a loose network-like structure, present abundant exposed sensing sites, oriented transmission of charges, and unimpeded pathways for H<sub>2</sub>S diffusion, which endow the cPcCo-B-aCNT hybrids with excellent sensing performance, in terms of sensitivity, reliability, reproducibility, and detection limit. The detection limit of the sensors composed of cPcCo-BaCNT hybrids towards H<sub>2</sub>S reaches the ppb-level at room temperature, which is about the same as the odor threshold level for humans. For the cPcCo-HQ-aCNT sensor, the response to  $H_2S$  varies linearly with respect to its concentration from 20 to 160 ppb and from 320 to 2560 ppb, with the highest gas response of 2.5% to 80 ppb  $H_2S$  and a low detection limit of 5 ppb. Furthermore, the linking molecules play a critical role in the sensitivity of H<sub>2</sub>S, as evidenced from the current-voltage characteristics. The systematic study developed here provides a valid way to fabricate other high-efficient H<sub>2</sub>S sensors.

> sensors, they still suffer from some drawbacks, such as poor gas-sensing selectivity, low response, high operating temperature and high power consumption.

> Metal phthalocyanines (MPcs), owing to their unique conjugated  $18\pi$ -electron structure, diversity of central atoms, and easily tailored functional groups at the outer phthalocyanine ring, are well-known organic thin film gas sensors.24-26 Many studies indicate that MPc-based sensors could work at room temperature with high sensitivity, short response time and good selectivity. For example, F. I. Bohrer et al. revealed that MPcs with different central atoms can be used as sensing materials to detection of volatile organic compounds (VOCs).27 S. Altun et al. disclosed that MPcs can serve as sensing materials for inorganic gases (such as SO<sub>2</sub>, CO and CO<sub>2</sub>) by regulating their substituted groups.28 Significantly, for MPc-based sensors, critical shielding and an operational environment are necessary owing to the intrinsically high impedance of MPcs or else the response and reproducibility of pristine MPc sensors would be relatively poor. In addition, pristine MPcbased sensors with compact film possess small accessible surface areas and less exposed active sites for sensing, which also limit the efficiency and sensitivity seriously. Hence, the current detection results of pristine MPc-based sensors are not as good as expected.

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To overcome the above-mentioned drawbacks, an effective solution is to introduce conductive agents.<sup>29,30</sup> Carbon nanotubes (CNTs) are one of the ideal conductive agents for enhanced gas sensing. Owing to the CNTs' unique one-dimensional structure, high electrical conductivity, excellent thermal stability and mechanical properties,31-34 electrons of MPc can be readily accepted by CNTs and then be transported under nearly ideal conditions along the tubular CNT axis.35 Therefore, the resistance change arising from the charge transfer between the adsorbed gas molecules and MPc/CNT hybrids becomes more obvious. Moreover, in the MPc/CNT sensors, CNTs are interlaced with one another forming a web-like structure, producing a large surface area on which more MPc molecules are exposed as active sites for high sensitivity. Actually, some MPc/CNT hybrids synthesized via non-covalent modification have been designed to detect dangerous gases, because the flat, planar aromatic structure of MPcs is ideal for  $\pi$ - $\pi$  stacking interactions with the sidewalls of CNTs.<sup>36-38</sup> Due to the synergistic effect of MPcs and CNTs, MPc/CNT hybrids really yield high efficiency at room temperature, often outperforming pristine MPc and CNTs in terms of sensitivity, selectivity, and response time.<sup>39,40</sup> However, due to the indefinable  $\pi$ - $\pi$  interactions and van der Waals force between MPcs and CNTs, it is difficult to control the architecture and properties of MPc/CNT hybrids, and the dispersion in the matrix of gas sensors accurately, further resulting in poor gas-sensing reproducibility and stability. Evidently, how to fabricate the MPc/CNT hybrids for efficient gas sensors is still one of the main themes of current research in this field.

Compared with non-covalent modification, covalent bonding directly to the surface of CNTs with MPcs, through a specific chemical reaction, offers accurate tailoring of the composition and architecture.<sup>41,42</sup> It has been proposed that appropriate linking molecules not only facilitate the combination of MPcs and CNTs, but also accelerate the charge transfer from MPcs to CNTs, and thus improve the gas sensing performance.<sup>35,43,44</sup> However, there are apparently very few studies focused on CNTs covalently bonded with MPcs for gas sensing, and fewer studies on their application in H<sub>2</sub>S gas sensors. Moreover, no systematic study has worked on the effect of linking molecules on the gassensing performance of MPc/CNT hybrids.

On the basis of the above consideration, in this work, acidified multi-walled carbon nanotubes (aCNTs) covalently bonded with tetra- $\beta$ -carboxyphenyloxyphthalocyanine cobalt( $\pi$ ) (cPcCo) via a condensation reaction in the presence of N,N'-dicyclohexylcarbodiimide (DCC), using hydroquinone (HQ), p-aminophenol (PAP), and p-phenylenediamine (PPD) as linking molecules (as show in Scheme 1), respectively have been used for H<sub>2</sub>S-sensing. As expected, compared with other H<sub>2</sub>S-sensing materials, the obtained hybrids (cPcCo-B-aCNT, B= HQ, PAP, and PPD) show enhanced sensitivity, response time, reproducibility and selectivity. In particular, the sensor composed of the cPcCo-HQ-aCNT hybrid shows the highest gas response of 2.5% to 80 ppb H<sub>2</sub>S, and a low detection limit of 5 ppb. Furthermore, the influence of linking molecules on the dispersion and H<sub>2</sub>S-sensing performance of the cPcCo-B-aCNT hybrids has also been systematically discussed.



Scheme 1 A schematic illustration of the synthesis procedure for cPcCo-B-aCNT hybrids.

## 2. Experimental

#### 2.1 Reagents

Multi-walled carbon nanotubes (CNTs, purity >95%, 5-15 µm in length, 10-20 nm in diameter) purchased from Shenzhen Nanotech Port Co., Ltd. were purified to remove impurities by the established methods.45,46 4-Nitrophthalonitrile (99% purity), phydroxybenzoic acid (99% purity) and DBU (98% purity) were purchased from Sigma-Aldrich Co. LLC. N,N'-Dicyclohexylcarbodiimide (DCC) (99% purity) and 4-dimethylaminopyridine (DMAP) (99% purity) were purchased from Aladdin Co. LLC. Ultrapure water (resistivity 18.2 M $\Omega$  cm) was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used in the whole experimental process. Acidified multi-walled carbon nanotubes (aCNTs) were prepared by a well-established method (see the ESI<sup>†</sup> for experimental details). Tetra-β-carboxyphenyloxyphthalocyanine cobalt(II) (cPcCo) was synthesized by the common template reaction of 4-(4-carboxyphenyloxy)phthalonitrile with anhydrous cobalt(II) chloride in the presence of 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU) (see the ESI<sup>+</sup> for experimental details). All other reagents in this work were of analytical grade and used without further purification.

#### 2.2 Preparation of cPcCo-B-aCNT hybrids

The cPcCo–HQ–aCNT hybrid was prepared by a two-step condensation reaction at room temperature using DCC as the condensation agent. Briefly, HQ (3.0 mmol) was dissolved in a solution of aCNTs (0.10 g) in anhydrous *N*,*N*-dimethylmethanamide (DMF) (20 mL). It was then sonicated at room temperature for 30 min. After that, DCC (0.30 g) and DMAP (0.050 g) were added and the mixture was sonicated at room temperature for another 30 min. The resulting black mixture was filtered through a 0.45  $\mu$ m polytetrafluoroethylene (PTFE) membrane filter, and washed continuously with methanol, acetic acid, 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, affording the HQ modified CNTs. Subsequently, cPcCo (0.20 g)

#### Paper

was condensed with the HQ modified CNTs in a similar fashion and using the same conditions, and finally the cPcCo-HQaCNT hybrid was obtained as a black powder. cPcCo-PAP-aCNT and cPcCo-PPD-aCNT hybrids were fabricated using similar procedures except for the replacement of HQ with PAP and PPD, respectively. As a control, aCNTs modified with cPcCo (cPcCo/ aCNTs) were synthesized by using a solution self-assembly method based on non-covalent interactions (see the ESI† for experimental details).

#### 2.3 Sensor assembling and sensing measurements

A complete description of the gold interdigitated electrodes (IDEs) and the gas sensor testing device was already reported in our previous study.<sup>38</sup>

To prepare gas sensors composed of cPcCo-B-aCNT hybrids, the as-prepared cPcCo-B-aCNT hybrids were dispersed in ethanol to obtain a uniform suspension of 1.0 mg mL<sup>-1</sup> by ultrasonication for 30 min, and then approximately 50 µL of the homogeneous dispersion was sprayed on the IDEs using an airbrush tool. To remove the solvent of the sensor and improve the electrical contact between the hybrids and the gold electrodes, the sensor devices were annealed in a vacuum oven for 2 h at 50 °C before sensing tests. For comparison, gas sensors, composed of the cPcCo/aCNT hybrid and aCNTs were also fabricated by similar procedures. For the sensor based on cPcCo, the as-prepared cPcCo was dissolved in acetone to obtain a 5.0 mg mL<sup>-1</sup> solution first, and then approximately 50  $\mu$ L of the solution was dispensed on the IDEs using a trace sampler (100 µL). The resulting sensor was dried in a vacuum oven at 50 °C for 2 h.

A typical sensing test cycle consisted of three sequential steps and in order to speed up the recovery of the sensor, a nonozone type mini ultraviolet (UV) lamp (10 V/3 W, 254 nm) was used in the course of removal of the gas. First, an air flow was introduced into the sensing test chamber to record a baseline. Then, a target gas with certified concentrations was injected to register sensor signals. Finally, the sensor was recovered in an air flow under UV light. A constant DC voltage of 0.5 V was applied to the electrode gap bridged by the hybrids and all measurements were performed at 28 °C  $\pm$  0.5 °C with a relative humidity of 60%  $\pm$  2%. In this study, sensitivity (*S*) is defined by the relative resistance change, as follows:

$$S = \frac{\Delta R}{R_0} \times 100\% = \frac{R_{\rm g} - R_0}{R_0} \times 100\%$$

where  $R_0$  is the sensor resistance in the initial air flow which was used as the background and  $R_g$  is the sensor resistance after being exposed to a certain concentration of target gas. Response and recovery times are defined as the time needed for 90% of total resistance change on exposure to the target gas and air, respectively.

#### 2.4 Characterization

FT-IR spectra were recorded on a Nicolet FT-IR NEXUS spectrometer (Thermo Scientific). The Raman spectra were acquired using a Raman spectrophotometer (HR800, HORIBA Jobin Yvon absorption spectra were recorded with a Lambda 35 UV/Vis spectrometer (Perkin-Elmer). Thermogravimetric (TG) analysis was performed on a TA Q 600 under a stream of nitrogen at a heating rate of 10 °C min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were performed with an AXIS ULTRA DLD. Scanning electron microscopy (SEM) images were recorded with a Hitachi S-4800 field emission scanning electron microscope operating at 15 kV. Transmission electron microscopy (TEM) images were obtained using a JEM-3010 electron microscope (JEOL) with an acceleration voltage of 300 kV. Nitrogen adsorption-desorption isotherms at 77 K were collected on a Micromeritics ASAP 2010 nitrogen adsorption apparatus. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area. The gaseous products collected after the cPcCo-HQ-aCNT sensor was exposed to H2S were monitored by gas chromatography-mass spectrometry (GC-MS, AGI-LENT, 6890-5973N) using a DB-5 column from 50 to 250 °C at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup> and a N<sub>2</sub> flow rate of 1 mL min<sup>-1</sup>. The current-voltage (I-V) characteristics of the fabricated sensors were measured using a Keithley 4200 semiconductor parameter analyzer with a two-point probe setup via sweeping the potential between -1 and +1 V under a 0.01 V s<sup>-1</sup> scan rate. Electrochemical impedance spectroscopy (EIS) was carried out on a CHI760D electrochemical working station (CH Instruments) at room temperature, the range of frequency was 0.01 Hz to 100 kHz and the excitation amplitude was 0.2 V.

Company) excited by a laser with 457.9 nm wavelength. UV/Vis

## 3. Results and discussion

#### 3.1 Characterization of cPcCo-B-aCNT hybrids

According to the design strategy, three cPcCo–B–aCNT hybrids were synthesized by a condensation reaction in the presence of DCC as the condensation agent. The typical FT-IR spectra of cPcCo, aCNTs, and cPcCo-HQ-aCNT hybrids are shown in Fig. 1A. The typical bands of the carboxyl group on aCNTs appear at 1720 cm<sup>-1</sup> (U C=O) and 3435 cm<sup>-1</sup> (U O-H).<sup>47,48</sup> cPcCo exhibits characteristic vibrations at 1599 cm<sup>-1</sup> ( $\upsilon$  C=C) and 1237 cm<sup>-1</sup> ( $\upsilon$  Ar–O–Ar). Compared with the FT-IR spectrum of cPcCo, two distinct peak-shifts (1513 cm<sup>-1</sup> and 1163 cm<sup>-1</sup>) appear in the spectrum of the cPcCo-HQ-aCNT hybrid, which may be ascribed to the interaction between the phthalocyanine macrocycle and CNT backbone.41,49 The covalent bonding of cPcCo with aCNTs was also evidenced by Raman spectra. As shown in Fig. 1B, the D-, G-, and D'-bands of the aCNTs appear at 1360, 1571, and 1610 cm<sup>-1</sup>, respectively, which can be attributed to the defects and disorder-induced modes, in-plane E2g zone-center mode, and the disorder in carbon nanotubes.50 In contrast to the case of aCNTs, the D- and G-bands of the cPcCo-HQ-aCNT hybrid, which appear at 1368 and 1580 cm<sup>-1</sup>, are found to be slightly shifted to the high wavenumbers. The  $I_{\rm G}/I_{\rm D}$  of the cPcCo-HQ-aCNT hybrid is almost the same as that of aCNTs (2.08 vs. 2.00). The results indicate that cPcCo has succeeded in bonding onto the surface of aCNTs via various linking molecules, and the attachment does not affect the structure of aCNTs.51,52



Fig. 1 (A) FT-IR spectra, (C) UV-Vis spectra, and (D) TGA profiles of cPcCo, aCNTs, and cPcCo–HQ–aCNTs hybrid; (B) Raman spectra of aCNTs, and cPcCo–HQ–aCNTs hybrid obtained at  $\lambda_{exc} = 457.9$  nm.

Fig. 1C shows the UV-Vis spectra of cPcCo, aCNTs and cPcCo-HQ-aCNTs hybrid in DMF, respectively. Apparently, the characteristic Q-band of cPcCo (664 nm) is observed in the UV-Vis spectrum of the cPcCo-HQ-aCNTs hybrid, accompanied by a red shift of about 10 nm, suggesting the charge transfer from the cPcCo ring to aCNTs.53,54 TG analysis under a N2 atmosphere was used to determine the content of cPcCo in the hybrids (Fig. 1D). In the range of 320-600 °C, the weight loss of cPcCo and aCNTs is about 31.53% and 6.98%, respectively, which originates from the destruction of the phthalocyanine peripheral substituent group and the residual amorphous carbon, and the decarboxylation of the oxidized species. For the cPcCo-HQaCNT hybrid, the weight loss is only 8.31% at the same temperature range.<sup>40,55</sup> Thus, a corrected weight loss of 1.33% can be obtained, which comes from cPcCo in the cPcCo-HQaCNT hybrid. Considering the actual amount of cPcCo chemically bonded to the surface of aCNTs, a real ratio of 4.22% (1.33%/31.53%) can be calculated. Meanwhile, the FT-IR, Raman, UV-Vis spectra and TGA analysis of cPcCo-PAP-aCNT and cPcCo-PPD-aCNT hybrids were also obtained (Fig. S1-S4<sup>+</sup>), illustrating that cPcCo-PAP-aCNT and cPcCo-PPD-aCNT hybrids were prepared successfully. The ratio of cPcCo in cPcCo-PAP-aCNTs and cPcCo-PPD-aCNTs is 4.10% and 4.38%, respectively, which are basically similar to that of the cPcCo-HQ-aCNT hybrid.

As a further proof, XPS measurements were performed, which could provide the chemical composition and states of surface elements. In the survey spectra of cPcCo–B–aCNT hybrids, N and Co species could be found, further revealing the reaction between cPcCo and aCNTs (Fig. S5†). The high-resolution XPS spectrum of N in the cPcCo–HQ–aCNT hybrid can be mainly deconvoluted into two sub-peaks located at about 398.9 and 400.1 eV, ascribed to the aza-bridging nitrogen and pyrrole nitrogen, respectively (Fig. 2A).<sup>56</sup> Significantly, a new peak at 401.60 eV can be obviously observed in both cPcCo–PAP–aCNT



**Fig. 2** High-resolution N1s XPS spectra (A) and C1s XPS spectra (B) of cPcCo-HQ-aCNT, cPcCo-PAP-aCNT and cPcCo-PPD-aCNT hybrids, respectively.

and cPcCo–PPD–aCNT hybrids, which issues from the nitrogen of the amide group (–NH–CO–) being used for bonding between the carboxyl and substituted amino (–NH<sub>2</sub>) groups.<sup>57</sup> Accordingly, the peaks at 286.2 eV assigned to the carbon of the amide group (–NH–CO–) are also observed in the C1s XPS spectra of cPcCo–PAP–aCNT and cPcCo–PPD–aCNT hybrids (Fig. 2B).<sup>58</sup> All these findings are indicative of the formation of a covalent bond between cPcCo and aCNTs using HQ, PAP, and PPD as the linking molecules, respectively.

The microstructures of the aCNTs and the cPcCo–B–aCNT hybrids were also characterized by SEM and TEM. The typical SEM images of aCNTs, cPcCo–HQ–aCNT, cPcCo–PAP–aCNT and cPcCo–PPD–aCNT hybrids are shown in Fig. 3A–D. After spraying on the IDEs, both aCNTs and cPcCo–B–aCNT hybrids appear as three-dimensional network-like structures. Compared with aCNTs, the film of the cPcCo–HQ–aCNT hybrid is more uniform and looser, due to better dispersion. In contrast, there are some "knots" in the cPcCo–PAP–aCNT and cPcCo–PPD–aCNT hybrids, which are mainly due to the presence of amino (–NH) groups in the cPcCo–PAP–aCNT and cPcCo–PPD–aCNT hybrids.

The amino group with a strong electron-donating nature not only effectively connects cPcCo and aCNTs, but also improves the polarity of the hybrids and enhances the intermolecular force, resulting in the re-aggregation of hybrids and generating the "knots". The influence of linking molecules on the dispersion of the cPcCo-B-aCNT hybrids in ethanol was also studied. As shown in Fig. 3G-J, aCNT and cPcCo-B-aCNT hybrids can disperse in ethanol well and form black mixtures after sonicating at room temperature for 10 minutes, which is very beneficial to fabricating uniform films by the spraying technology for use as gas sensors. However, after standing for 3 days at room temperature, aCNT and cPcCo-PPD-aCNT hybrid slowly settled down and the ethanol became clear. On extending the standing time to 15 days, the cPcCo-PAP-aCNT hybrid precipitated at the bottom of the container; while the cPcCo-HQ-aCNT hybrid still remained as a good dispersion even after standing for 60 days. Evidently, the long-term dispersion and stability of cPcCo-HQaCNTs can be attributed to the covalent grafting of cPcCo onto the surface of aCNTs via the linking molecule HQ. A discontinuous and irregular layer appears outside the distinct core and walls of carbon nanotubes (Fig. 3E and F), which probably arises from cPcCos coated onto aCNTs through covalent bonds.



Fig. 3 (A–D) The typical SEM image of aCNTs (A), cPcCo–HQ–aCNT (B), cPcCo–PAP–aCNT (C) and cPcCo–PPD–aCNT hybrids (D), respectively; (E and F) the TEM images of cPcCo–HQ–aCNT hybrid; (G–J) optical photographs of the equivalent aCNT and cPcCo–B–aCNT hybrids dispersed in ethanol after sonicating at room temperature for 10 minutes (G), and after standing at room temperature for 3 days (H), 15 days (I), and 60 days (J). ((a)–(d): aCNT, cPcCo–HQ–aCNT, cPcCo–PAP–aCNT, and cPcCo–PPD–aCNT hybrids, respectively).

Meanwhile, cPcCo–B–aCNT hybrids show a large surface area of 132.7–135.3 m<sup>2</sup> g<sup>-1</sup>, being larger than that of the aCNT hybrid (114.0 m<sup>2</sup> g<sup>-1</sup>, Fig. S6†). Such an increase in surface area is mainly due to covalent grafting of cPcCo onto the surface of aCNTs. Due to the easily accessible active sites for gas adsorption, and the permeable channels for diffusion of gas molecules, cPcCo–B–aCNT hybrids are conducive to accelerating the interaction between the hybrids and adsorbed gas molecules, giving rise to the high sensing activity.<sup>10</sup>

#### 3.2 H<sub>2</sub>S sensing properties of cPcCo-B-aCNT hybrids

To assess the H<sub>2</sub>S-sensing activity of cPcCo-B-aCNT hybrids, gas-sensor devices were fabricated using IDEs, according to the experimental part. A constant DC voltage of 0.5 V was applied to the electrode gap (50  $\mu$ m) covered by the hybrids. The signal resistor was continuously recorded, as the sensor sample was subjected to the target gas exposure in an air-tight chamber, and then recovered under UV light at room temperature. As a control, the sensing response of aCNTs and cPcCo towards H<sub>2</sub>S were also studied. The detailed dynamic responses of the sensors upon repeated H<sub>2</sub>S exposure/removal cycles are shown in Fig. 4A. Nine cycles were successively recorded at room temperature, corresponding to H<sub>2</sub>S concentrations from 20 to 5120 ppb. It can be seen that the response intensities of all the sensors increase as the concentration of H<sub>2</sub>S gas is increased. Although the cPcCo sensor displays fast response and recovery, its response intensity is so weak that no response can be observed at less than 320 ppb H<sub>2</sub>S, while for the aCNT sensor, both the response intensity and the recovery time are poor. By contrast, the cPcCo-B-aCNT sensors generate remarkable responses towards H<sub>2</sub>S. The relationship of the response of cPcCo, aCNT, and cPcCo-B-aCNT sensors to the concentration

of  $H_2S$  was also investigated (as shown in Fig. 4B), and all cPcCo–B–aCNT sensors exhibit two good linear responses (Fig. S7†). In particular, the cPcCo–HQ–aCNT sensor shows the best sensor response, 0.0325% per ppb  $H_2S$  for concentrations ranging from 20 to 160 ppb, and 0.0061% per ppb  $H_2S$  for



Fig. 4 (A) Response of CPCCo, aCNT, CPCCO-HQ-aCNT, CPCCO-PAP-aCNT and CPCCO-PPD-aCNT sensors upon exposure to varying concentrations of  $H_2S$ ; (B) relationship of the response of CPCCo, aCNT, CPCCO-HQ-aCNT, CPCCO-PAP-aCNT and CPCCO-PPD-aCNT sensors to varying concentrations of  $H_2S$ ; (C) response of CPCCO-HQ-aCNT sensor exposure to 320 ppb  $H_2S$  and recovery under UV light or without UV light; (D) ten sensing cycles of the CPCCO-HQ-aCNT sensor to 80 ppb  $H_2S$  (inset: reproducibility characteristic of the CPCCO-HQ-aCNT sensor to 80 ppb  $H_2S$  at different durations).

concentrations ranging from 320 to 2560 ppb, and the lowest theoretical detection limit (S/N = 3) for H<sub>2</sub>S is approximately 5 ppb (Table S1†). The ppb-level sensing of cPcCo-HQ-aCNTs, reaching the odor threshold level for humans, is superior to most of the reported H<sub>2</sub>S sensors (Table S2†).

It is clear that the synergistic effect between cPcCo and aCNTs enhances the sensing performance. cPcCo covalently bonded on the surface of aCNTs offers more sensing sites for H<sub>2</sub>S reaction, and aCNTs as a conductive agent can accelerate the charge transfer. It can further be evidenced by the H<sub>2</sub>S response of the cPcCo/aCNT sensor prepared by non-covalent interactions. Compared to the cPcCo-B-aCNT hybrids, the cPcCo/aCNT sensor shows a lower intensity of response and higher limit of detection (Fig. S8 and Table S1<sup>†</sup>). Consequently, the covalent linkage is conducive to the efficient combination of MPcs and CNTs, and thus facilitates the charge transfer from MPcs to CNTs and improves the gas sensing performance. In addition, for all the cPcCo-B-aCNT hybrids, the surface area and cPcCo loading are similar, but the cPcCo-HQ-aCNT sensor displays the greatest response among the hybrids, suggesting that the linking molecule plays an important role in H<sub>2</sub>S sensing. The influence of linking molecules on the sensing property will be discussed below.

The effect of UV irradiation on the recovery property of the cPcCo-HQ-aCNT sensor was also studied. In Fig. 4C, the cPcCo-HQ-aCNT sensor was exposed to 320 ppb of H<sub>2</sub>S, and then recovered with or without UV radiation at room temperature. The response time of the cPcCo-HQ-aCNT sensor was about 58 seconds, and the recovery time was about 614 seconds under UV radiation; nevertheless, the recovery time lengthened significantly without UV radiation. The results illustrate that the recovery of the cPcCo-HQ-aCNT sensor strongly depends on UV radiation. In this case, the photogenerated electrons can react with O<sub>2</sub> in air producing adsorbed oxygen, and then the residual holes form an accumulation layer on the surface of cPcCo-HQ-aCNTs.59 Therefore, the resistance of cPcCo-HQ-aCNTs reduces and the sensor is recovered. To further verify the reproducibility and reliability, ten response cycles of the cPcCo-HQ-aCNT sensor to 80 ppb H<sub>2</sub>S at room temperature were recorded (Fig. 4D). It can be seen that, with the on-off H<sub>2</sub>S signal, the sensor shows a fast response time (less than 30 s) and recovery time (less than 520 s under UV radiation), and there is no change in the ten continuous cycles. The long-term stability of the cPcCo-HQ-aCNT sensor was also evaluated over 60 days by determining the response to 80 ppb H<sub>2</sub>S and storing in air at room temperature when not in use, and the results are shown in the inset of Fig. 4D. A slight response drop (only about 10%) could be observed after storing for 60 days. Clearly, the cPcCo-HQ-aCNT sensor has good stability and reproducibility, which is crucial for further applications.

For gas sensors, reduced cross-sensitivity from intervening gases is one of the important indexes for practical application. To probe the selectivity of the cPcCo–B–aCNT sensors, the representative gases in air and volatile organic compounds (VOCs) were separately injected into the test chamber in turns at room temperature (as shown in Fig. 5 and S9†). Compared to the aCNT sensor, all the prepared cPcCo–B–aCNT sensors show good selectivity, especially the cPcCo–HQ–aCNT sensor. It



Fig. 5 Cross-sensitivities to various gases for the aCNT sensor (A) and cPcCo-HQ-aCNT sensor (B) 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.

should be pointed out that the cPcCo–B–aCNT sensors exhibit high responses to  $H_2S$  and low responses to  $NH_3$ , NO and  $NO_2$  at the same concentration (2.56 ppm), which is usually not achieved easily. Moreover, in contrast to  $H_2S$  and  $NH_3$ , the resistances of cPcCo–B–aCNT sensors reduce when they are exposed to the oxidizing atmospheres, NO and  $NO_2$ . As is well known, both cPcCo and aCNTs are typical p-type semiconductors. According to the charge-transfer mechanism, NO (or  $NO_2$ ) can attract the electrons from cPcCo–B–aCNT hybrids and generate more holes in the hybrids, leading to the reduced resistance. Further, the cPcCo–HQ–aCNT sensor shows a negligible response to VOCs even at high concentrations (1000 ppm). Therefore, it is promising as a  $H_2S$  sensor to achieve quantitative detection of  $H_2S$  in an indoor atmosphere, industrial petroleum/gas, automobile exhaust gas, and so on.

#### 3.3 H<sub>2</sub>S sensing mechanism of the cPcCo-B-aCNT sensors

The sensitivity of the cPcCo–B–aCNT sensors towards  $H_2S$  accords with the classical charge-transfer theory. In general, the sensing effect is most likely to occur at the cPcCo layer, which covalently bonds onto the surface of aCNTs.<sup>60</sup> Herein,  $H_2S$  interacts with the main adsorbed oxygen species ( $O_2^-$ ) at room temperature,<sup>61</sup> and releases a large number of electrons as indicated in the following equation:

 $2H_2S(g) + 3O_2^-(ads) \rightarrow 2H_2O(g) + 2SO_2(g) + 6e^-$ 

The electrons generated are trapped by the cPcCo–B–aCNT hybrids through the phthalocyanine layer (layer 2) and linking-

molecule layer (layer 1) in sequence. During the electrontransfer process, electrons recombine with holes and decrease the density of the hole-accumulation layer, which results in increased resistance, as illustrated in Scheme 2.

To validate the H<sub>2</sub>S sensing mechanism, the chemical composition and states of surface elements in the cPcCo-HQaCNT sensor after exposure to H<sub>2</sub>S were probed by XPS measurement (as shown in Fig. S10<sup>†</sup>). Apparently, after exposure to H<sub>2</sub>S at room temperature, two weak peaks ascribed to S2s ( $\sim$ 225 eV) and S2p (156–175 eV) can be observed in the XPS survey spectrum of the cPcCo-HQ-aCNT sensor. In the corresponding S2p XPS spectrum, the two binding energies of 168.1 eV and 164.2 eV belong to the characteristic peaks of SO<sub>2</sub> and H<sub>2</sub>S, respectively.<sup>9,15</sup> As further evidence, the distinct signal of SO<sub>2</sub> appears in the GC-MS spectra (Fig. S11<sup>†</sup>). These results confirm that H<sub>2</sub>S is oxidized to SO<sub>2</sub>, in accordance with the above sensing mechanism. In addition, compared with NH<sub>3</sub>, NO, NO<sub>2</sub>, and VOCs, the excellent selectivity of cPcCo-B-aCNT hybrids for H<sub>2</sub>S can be mainly ascribed to the strong interaction between H<sub>2</sub>S molecules and the adsorbed oxygen ions (e.g.  $O^{2-}$ , O<sup>-</sup>, and O<sub>2</sub><sup>-</sup>) on the surfaces of the cPcCo-B-aCNT hybrids.<sup>62</sup>

As mentioned above, the linking molecules dramatically influence the dispersion and sensing performance of the cPcCo-B-aCNT hybrids. In order to explore the effect of the linking molecules, the I-V characteristics of the cPcCo-B-aCNT sensors with the same mass loading on IDEs were investigated (Fig. 6A). The linearity and symmetry of I-V curves suggest an ohmic contact between the samples and gold electrodes. Evidently, the device current of various hybrids at the same voltage decreases in the order aCNTs > cPcCo-HQ-aCNTs > cPcCo-PAP-aCNTs > cPcCo-PPD-aCNTs. Low current means the sensor has a relatively high resistance. For cPcCo-B-aCNT hybrids, the decrease in device current is possibly caused by the intrinsically high resistance of cPcCo, and the donation of electrons from the p-type cPcCo to the p-type aCNT backbone by means of linking molecules.63 Due to the similar cPcCo content, the distinct difference in device current of the three cPcCo-B-



Scheme 2 A schematic illustration of the gas sensing mechanism of cPcCo-B-aCNT sensors upon interaction with  $H_2S$ .



Fig. 6 (A) I-V curves and (B) Nyquist plots of aCNT and various cPcCo-B-aCNT sensors.

 Table 1
 Fitted impedance parameters of cPcCo-HQ-aCNT, cPcCo-PAP-aCNT and cPcCo-PPD-aCNT electrodes

Samples	$R_{\rm b}\left(\Omega\right)$	$C \left( \mathrm{F} \ \mathrm{cm}^{-2} \right)$	$R_{\rm ct}\left(\Omega\right)$
cPcCo–HQ–aCNT cPcCo–PAP–aCNT cPcCo–PPD–aCNT aCNT	4.21 4.46 4.56 4.70	$\begin{array}{l} 5.82 \times 10^{-7} \\ 5.49 \times 10^{-7} \\ 4.59 \times 10^{-7} \\ 4.35 \times 10^{-7} \end{array}$	12.50 15.36 17.45 20.99

aCNT hybrids is ascribed to the different linking molecules. Amino (–NH) groups have stronger electron-donating capability than –OH groups.<sup>64</sup> Relative to HQ, the linking molecules PAP and PPD containing –NH groups can provide more electrons to combine with the holes in p-type semiconductors of cPcCo and aCNTs. The combination of electrons and holes can reduce the carrier concentration of the system, leading to further increase in the resistances of cPcCo–PAP–aCNT and cPcCo–PPD–aCNT hybrids. Hence, their responses towards H<sub>2</sub>S are not as good as that of the cPcCo–HQ–aCNT hybrid (Fig. 4A).

The EIS of the cPcCo-HQ-aCNT, cPcCo-PAP-aCNT and cPcCo-PPD-aCNT electrodes were also measured to investigate their kinetic processes (Fig. 6B). The Nyquist plots are fitted by an appropriate electric equivalent circuit (insets of Fig. 6B),65 and the obtained impedance parameters are given in Table 1. Here,  $R_{\rm b}$  is the uncompensated bulk resistance of the electrolyte, separator and electrode,  $R_{\rm ct}$  is the charge-transfer resistance at the active material interface, and C is the constant phase angle element, involving double layer capacitance. It is clear that the values of  $R_{\rm b}$  and  $R_{\rm ct}$  are 4.21  $\Omega$  and 12.50  $\Omega$  for cPcCo-HQ-aCNTs, which are lower than those of cPcCo-PAPaCNTs ( $R_b = 4.56 \Omega$  and  $R_{ct} = 15.36 \Omega$ ), cPcCo–PPD–aCNTs ( $R_b =$ 4.60  $\Omega$  and  $R_{\rm ct}=$  20.99  $\Omega$ ) and aCNTs ( $R_{\rm b}=$  4.70  $\Omega$  and  $R_{\rm ct}=$ 20.99  $\Omega$ ). Both  $R_{\rm b}$  and  $R_{\rm ct}$  are related to the electrode's conductivity and the electron transportation for the gas sensor. The lower the values of  $R_{\rm b}$  and  $R_{\rm ct}$ , the stronger the electron transport. Therefore, the cPcCo-HQ-aCNT sensor displays a higher sensing response and lower detection limit than the other sensors.

### 4. Conclusions

A series of cPcCo-B-aCNT hybrids were successfully synthesized by covalent bonding using HQ, PAP, and PPD as linking molecules. Compared to many reported H<sub>2</sub>S sensors, the obtained sensors show ppb-level sensing towards H<sub>2</sub>S at room temperature. Among them, the cPcCo-HQ-aCNT sensor shows high sensitivity (2.5% to 80 ppb H<sub>2</sub>S with a detection limit of 5 ppb), fast response/recovery, and excellent stability, reproducibility and selectivity towards H<sub>2</sub>S. The significant enhancement in H<sub>2</sub>S sensing is associated with multiple advantages such as the unique structure and characteristics. First, the 3D loose structure not only provides more active sites for the reaction between the adsorbed O<sub>2</sub><sup>-</sup> and H<sub>2</sub>S, but also has unimpeded pathways for H<sub>2</sub>S diffusion and transport. Second, as the conductive agent, aCNTs can quickly capture the generated electrons, leading to a fast and sensitive response. In this system, the electron-donating capability of the linking molecules has a great influence on the H<sub>2</sub>S-sensing performance. The electrons coming from the linking molecule can combine with the holes of aCNTs and cPcCo, which can reduce the carrier concentration of the system and increase the system's resistance.

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