

An Organocobalt–Carbon Nanotube Chemiresistive Carbon Monoxide Detector

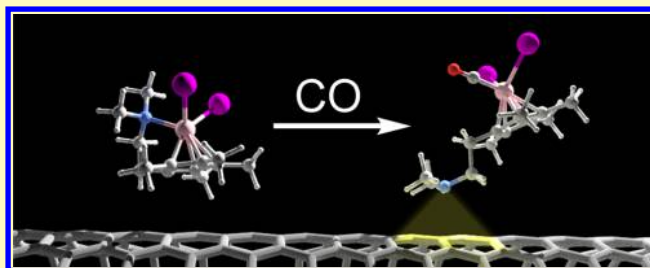
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S Supporting Information

ABSTRACT: A chemiresistive detector for carbon monoxide was created from single-walled carbon nanotubes (SWCNTs) by noncovalent modification with diiodo($\eta^5\text{-}\eta^1\text{-}[2\text{-(}N,N\text{-dimethylamino)ethyl-2,3,4,5-tetramethylcyclopentadienyl}]$ -cobalt(III) ($[\text{Cp}^*\text{CoI}_2]$), an organocobalt complex with an intramolecular amino ligand coordinated to the metal center that is displaced upon CO binding. The unbound amino group can subsequently be transduced chemiresistively by the SWCNT network. The resulting device was shown to have a ppm-level limit of detection and unprecedented selectivity for CO gas among CNT-based chemiresistors. This work, the first molecular-level mechanistic elucidation for a CNT-based chemiresistive detector for CO, demonstrates the efficacy of using an analyte's reactivity to produce another chemical moiety that is readily transduced as a strategy for the rational design of chemiresistive CNT-based detectors.

KEYWORDS: carbon monoxide, carbon nanotubes, cobalt, chemiresistor, gas sensor



The notoriously odorless, colorless, yet highly toxic gas carbon monoxide, produced from incomplete combustion of carbon-based fuels, poses a significant global toxicological threat¹ as the most common cause of death and injury by poisoning worldwide.^{2,3} Although detectors for CO are commercially available, there is still a need for electronic detectors that are small, low-powered, and inexpensive enough to be used as massively deployable distributed detectors.

Carbon nanotube (CNT)-based chemiresistors offer an opportunity to achieve these desirable attributes for CO detection. Like earlier optochemical detectors that changed color upon exposure to CO,⁴ CNT chemiresistors are inexpensive to fabricate and have low power and temperature requirements for operation. They also offer advantages over color-based indicators such as facile integration into electronic systems (e.g., alarms, remediation), the potential for quantitation, and freedom from line-of-sight observation.

Previous studies, however, show both theoretically^{5,6} and experimentally^{7–9} that the resistance of pristine carbon nanotubes is not perturbed by the presence of carbon monoxide, which does not engage in charge transfer with CNTs.^{10,11} Some theoretical studies, though, suggest that deformed⁶ or doped^{6,12,13} CNTs may be competent CO detectors. Additionally, there is experimental evidence for CO detection by oxidatively damaged CNT resistors bearing carboxylic acid moieties,^{8,9} CNTs dispersed in polyaniline^{14,15} or WO_3 ,¹⁶ and CNTs decorated with metallic¹⁷ or metal oxide nanoparticles.¹⁸

Although literature precedent exists for CNTs in electronic detectors for CO, a system based on CNTs functionalized with

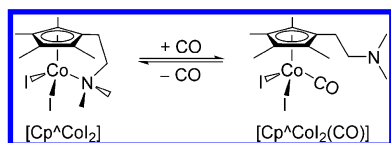
a discrete small molecule has yet to be reported. Indeed, the ill-defined nature of a nonmolecular system can hamper mechanistic elucidation. For example, in 2013, Zhang et al. reported a “CuCl”-CNT based CO detector but did not offer any experimentally substantiated mechanisms for the observed changes in resistance.¹⁹ Comparatively, a system based on a well-defined small molecule can be more readily understood using spectroscopic and computational tools available to the molecular chemist.

We hypothesized that a carbon nanotube-based chemiresistive detector for CO could be effected by designing a system that upon a highly selective reaction with CO would produce a chemical species capable of eliciting strong chemiresistive responses in CNTs such as ammonia or its derivatives.^{10,20–22} To this effect, we fabricated chemiresistors from CNTs noncovalently functionalized with diiodo($\eta^5\text{-}\eta^1\text{-}[2\text{-(}N,N\text{-dimethylamino)ethyl-2,3,4,5-tetramethylcyclopentadienyl}]$ -cobalt(III) ($[\text{Cp}^*\text{CoI}_2]$), originally reported by Jutzi et al. to reversibly coordinate CO with concomitant liberation of its intramolecular tertiary amino ligand from the metal center as shown in Scheme 1,²³ which can subsequently be transduced by the CNT network. The result, herein described, is the first example of a chemiresistive detector for CO based on CNTs functionalized with a discrete molecular species with a well-defined, experimentally supported molecular mechanism for CO detection. Furthermore, this strategy, using the analyte of

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Scheme 1. Reversible CO Binding to $[\text{Cp}^{\wedge}\text{CoI}_2]$ 

interest to produce a chemical species that induces a resistance change in the native CNT network, represents a new paradigm in the rational design of CNT-based chemiresistors.

We synthesized $[\text{Cp}^{\wedge}\text{CoI}_2]$ according to literature procedures.^{23,24} Jutzi et al. note that a significant visible green-to-purple color change is observed upon $[\text{Cp}^{\wedge}\text{CoI}_2]$ binding to CO. We also observe this color change upon sparging a solution of $[\text{Cp}^{\wedge}\text{CoI}_2]$ in CHCl_3 with 1 atm CO gas as shown in the visible absorbance spectra displayed in Figure 1.

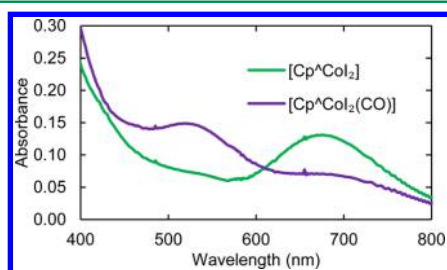


Figure 1. Visible absorbance spectra of $[\text{Cp}^{\wedge}\text{CoI}_2]$ in CHCl_3 before and after addition of 1 atm CO gas.

The original report of $[\text{Cp}^{\wedge}\text{CoI}_2]$ characterizes its CO adduct using IR, ^1H and ^{13}C NMR spectroscopies, which were used as evidence for the amine-dissociated structure of $[\text{Cp}^{\wedge}\text{CoI}_2(\text{CO})]$ (Scheme 1). However, Jutzi et al. were unable to obtain direct structural evidence by X-ray crystallographic structural determination for the purported amine dissociation upon binding of CO because $[\text{Cp}^{\wedge}\text{CoI}_2(\text{CO})]$ is only stable under 1 atm CO, which also hampered our efforts to obtain diffraction-quality single crystals.

To support that $[\text{Cp}^{\wedge}\text{CoI}_2(\text{CO})]$ with a free amine is the product of $[\text{Cp}^{\wedge}\text{CoI}_2]$ reacting with CO, we performed molecular calculations using density functional theory (DFT). The forward reaction depicted in Scheme 1 is calculated to be moderately exergonic with $\Delta G_{\text{rxn}} = -2.10$ kcal/mol. Using the relation $\Delta G_{\text{rxn}} = -RT \ln K_{\text{eq}}$, the predicted K_{eq} is 34.4. These predictions are in remarkable agreement with the experimental observations made by Jutzi et al. of (1) spontaneous partial ($\sim 90\%$ by ^1H NMR in CDCl_3) conversion of $[\text{Cp}^{\wedge}\text{CoI}_2]$ to $[\text{Cp}^{\wedge}\text{CoI}_2(\text{CO})]$ under 1 atm of CO and (2) instability of the adduct upon removal of CO from the reaction headspace. Alternative CO adduct geometries with bound amine and slipped cyclopentadienyl or dissociated I^- ligands were calculated to be thermodynamically uphill versus $[\text{Cp}^{\wedge}\text{CoI}_2]$ and free CO. These results support the structural assignment by Jutzi et al. of $[\text{Cp}^{\wedge}\text{CoI}_2(\text{CO})]$ based on NMR spectroscopy.

We fabricated the chemiresistors from a suspension of 0.25 mg of single-walled CNTs (SWCNTs) and 1.0 mg of $[\text{Cp}^{\wedge}\text{CoI}_2]$ in a mixture of 0.80 mL of 1,2-dichlorobenzene (DCB), 0.20 mL of CHCl_3 , and 50 μL of halocarbon oil 27 (HC27). DCB is known to be a moderately good solvent for the suspension of CNTs but only marginally solubilizes $[\text{Cp}^{\wedge}\text{CoI}_2]$; the CHCl_3 was added to fully solubilize the $[\text{Cp}^{\wedge}\text{CoI}_2]$. HC27, a high-boiling liquid polymer that remains

even after in vacuo removal of DCB and CHCl_3 , provides a liquid matrix for the active material, which we found to be as essential to a functional device as $[\text{Cp}^{\wedge}\text{CoI}_2]$. We hypothesize that HC27 allows for $[\text{Cp}^{\wedge}\text{CoI}_2]$ to engage in its solution-state reactivity with CO in the device, which we do not observe in its solid state.

Once prepared, the mixture was sonicated briefly at room temperature and then drop-cast between gold electrodes (1 mm gap) on glass microscope slides. The solvent was removed in vacuo at room temperature. The application of the suspension followed by in vacuo removal of the solvent was repeated until the resistance across the SWCNT network reached 10–100 k Ω as measured by an ohmmeter.

We calibrated the responses of the devices to concentrations of CO gas physiologically relevant to acute CO toxicity. For these measurements performed in N_2 for control purposes, the device was enclosed in a PTFE chamber, and the gold electrodes were attached to a potentiostat. Mass flow controllers were used to introduce either N_2 or CO diluted in N_2 to the device at a constant flow rate while the potentiostat applied a constant potential of 0.100 V across the electrodes and recorded the current over time. The negative change in current resulting from exposure to CO gas ($-\Delta G$) was divided by the initial current (G_0) to give change in conductance ($-\Delta G/G_0$), which was taken as the device's response.

The responses of the chemiresistors to various concentrations of CO gas are summarized in Figure 2a, which shows the average responses to 60 s exposures of triplicate devices. The responses to CO as a function of concentration are fit empirically with a second-order polynomial. Figure 2b displays the baseline-corrected conductance traces of three devices and their average responding to 60 s doses of various concentrations of CO gas. Figure 2c shows the conductance traces for three devices and their average exposed to 3000 ppm of CO in N_2 for 60 s with extended recovery time. The devices display sluggish reversibility; 1090 s elapse between maximum and half-maximum response, which could possibly be ameliorated by heating but would require additional power input.²⁵ With respect to reversibility, these devices behave in a manner similar to what we previously reported for a SWCNT-based ammonia chemiresistive detection system.²⁶

The limit of detection (LOD) for these devices is 90 ppm of CO, calculated as the concentration at which the signal exceeds three times the standard deviation of the baseline. Although the devices were not capable of detecting 50 ppm of CO, the OSHA PEL for an 8 h period, even after extended exposure, an LOD of 90 ppm for a relatively rapid 60 s exposure is already sufficient to detect concentrations of CO at which it is acutely toxic enough to be fatal (600–1000 ppm).²⁷ The active sensing composite is no longer functional upon omission of either HC27 or $[\text{Cp}^{\wedge}\text{CoI}_2]$; the resulting devices give no discernible chemiresistive response to 3000 ppm of CO.

Jutzi et al. note that $[\text{Cp}^{\wedge}\text{CoI}_2]$ reacts selectively with CO over its close analog C_2H_4 ,²³ and indeed, this selectivity appears to translate to the $[\text{Cp}^{\wedge}\text{CoI}_2]$ -based chemiresistor. Figure 3 shows the chemiresistive responses of quadruplicate $[\text{Cp}^{\wedge}\text{CoI}_2]$ -SWCNT devices to 0.3% CO diluted in N_2 in comparison to their responses to other gases at comparable concentrations also diluted in N_2 . The responses to these other gases, such as acetylene and ethylene, which have electronic similarities to CO and are common interferents for CO, and hydrogen, which is also a known interferent for electrochemical CO detectors, are negligible. Among previously reported CNT-

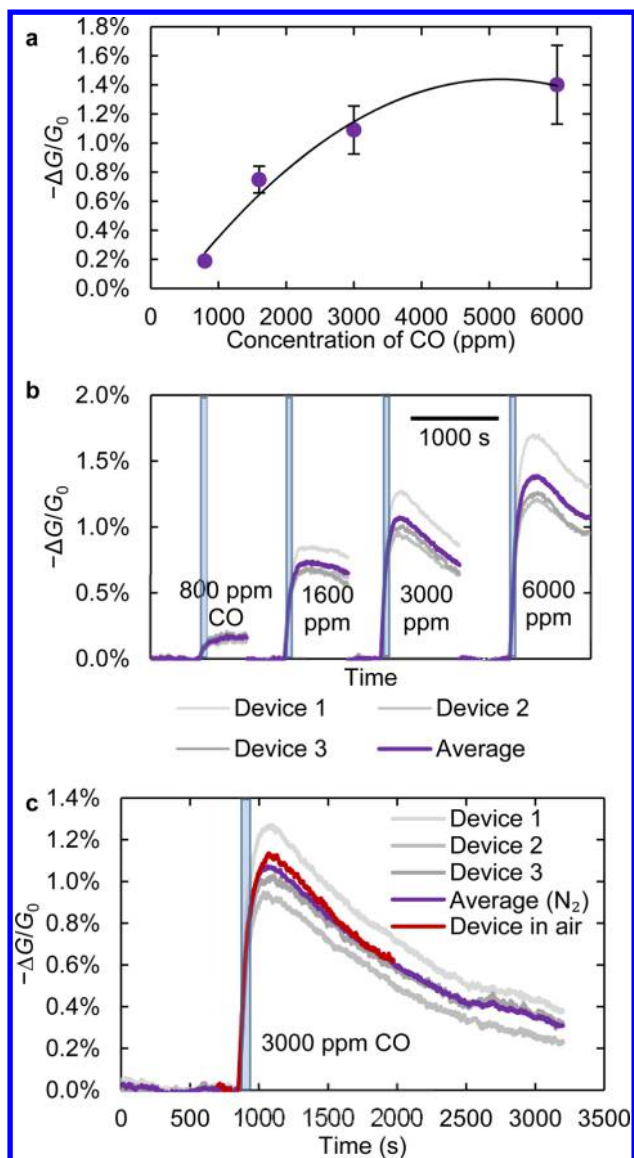


Figure 2. (a) Average conductance changes of three $[Cp^CoI_2]$ -SWCNT chemiresistive detectors in response to 60 s exposures to various concentrations of CO gas diluted in N_2 (quadratic fit); (b) conductance traces of $[Cp^CoI_2]$ -SWCNT chemiresistors to 60 s exposures (marked by blue boxes) of various concentrations of CO gas diluted in N_2 ; (c) conductance trace of three $[Cp^CoI_2]$ -SWCNT chemiresistors to 60 s exposure to 3000 ppm of CO in N_2 and one in air.

based electronic CO detectors, all of which are based on functionalization with nonmolecular chemical species, this level of demonstrated selectivity for CO is unprecedented.

Additionally, Figures 2c and 3 show that dilution of CO in air at 10% relative humidity (RH) rather than in N_2 at 3% RH does not significantly affect the chemiresistive response, suggesting that the devices tolerate both O_2 and modest levels of moisture. Prolonged testing of devices over the course of a few days or testing at 75% RH significantly impaired the magnitude of current decrease upon exposure to CO. This loss of performance may be due to movement of material such as aggregation of the SWCNTs facilitated by the presence of HC27 in the device, chemical instability of the composite, or loss of HC27 to evaporation over time. These general

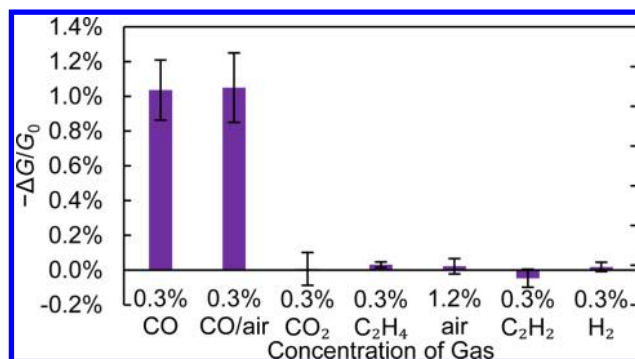


Figure 3. Average conductance changes of four $[Cp^CoI_2]$ -SWCNT chemiresistors in response to 60 s exposures to various gases diluted in N_2 unless otherwise indicated. Error bars represent 1 standard deviation across the four devices.

considerations continue to be a fundamental challenge in CNT-based sensors.

In this CO detection scheme, the reaction of CO with $[Cp^CoI_2]$ liberates an amine group, which can subsequently engage in charge transfer (electron donation) with CNTs²⁸ as suggested by previous theoretical^{29–31} and experimental³² studies, thus increasing their resistance. Therefore, we sought to confirm by Raman spectroscopy that charge transfer to the SWCNT occurs upon CO exposure. NH_3 has been noted to induce a downshift in the D band in the Raman spectrum of SWCNTs upon adsorption.³³ Indeed, we observe a downshift in the D band of the Raman spectrum of the $[Cp^CoI_2]$ -SWCNT material upon exposure to 1 atm CO, 1318 to 1316 cm^{-1} (Figure S3). No shift is observed upon exposure to 1 atm CO in the absence of $[Cp^CoI_2]$ (Figure S2). These spectroscopic measurements suggest that CO does liberate the amine group from the metal center of $[Cp^CoI_2]$, making it available for charge transfer to the SWCNTs.

In summary, we have rationally constructed a chemiresistive detector for CO gas from SWCNTs and $[Cp^CoI_2]$, which reacts with CO as shown in Scheme 1. The tertiary amine arm is then available to participate in charge transfer to the CNTs, leading to a marked increase in resistance. The resulting inexpensive, low-power device can detect CO at concentrations relevant to its acute toxicity with exposure times as short as 1 min; efforts to improve further on the sensitivity using ternary mixtures are ongoing. The device also demonstrates exquisite selectivity for CO unmatched by any previously reported CNT-based chemiresistor. We demonstrate that designing a system wherein reaction with a target analyte is coupled to the production of a chemical moiety that is strongly detected by CNTs is an effective approach for the development of CNT-based chemiresistive detectors. Additionally, due to the discrete molecular nature of this system, we are able to describe and experimentally support a well-defined, molecular mechanism for the first time in a CNT-based detector for CO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssensors.6b00005.

Device preparation, computational details, gas detection measurements, and spectroscopic and microscopic characterization (PDF)

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Notes

The authors declare the following competing financial interest(s): The authors are seeking patent protection on this technology.

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