Amine Sensors

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Single-Walled Carbon Nanotube/Metalloporphyrin Composites for the Chemiresistive Detection of Amines and Meat Spoilage**

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Abstract: *Chemiresistive detectors for amine vapors were made from single-walled carbon nanotubes by noncovalent modification with cobalt meso-arylporphyrin complexes. We show that through changes in the oxidation state of the metal, the electron-withdrawing character of the porphyrinato ligand, and the counteranion, the magnitude of the chemiresistive response to ammonia could be improved. The devices exhibited sub-ppm sensitivity and high selectivity toward amines as well as good stability to air, moisture, and time. The application of these chemiresistors in the detection of various biogenic amines (i.e. putrescine, cadaverine) and in the monitoring of spoilage in raw meat and fish samples (chicken, pork, salmon, cod) over several days was also demonstrated.*

For health and economic reasons, there is interest from meat providers and consumers in sensors to monitor its spoilage.[1] A detector for meat spoilage could prevent both unnecessary discard and the consumption of unsafe meat. One of the most salient markers of meat decomposition is the formation of biogenic amines (BAs). Among the most common BAs in food are putrescine (butane-1,4-diamine) and cadaverine (pentane-1,5-diamine). BAs are formed through microbial enzymatic decarboxylation of amino acids[2] and by amination of carbonyls.[3]

Many literature reports describe analytical methods for monitoring meat spoilage that rely on detection of amines or total volatile basic nitrogen (TVBN). Strategies for the detection of BAs include chromatography,[3] spectrometry,[4] electrophoresis,[5] colorimetry,[6] mass balance,[7] chemiluminescence,[8] and electrochemistry.[9] However, all of these strategies suffer from one or more drawbacks: extensive sample preparation prior to analysis; expensive, cumbersome instrumentation requirements with high power consumption; a requirement for highly trained personnel to operate the instrumentation; and line of sight is required to read the output.

Electronic sensors such as chemiresistors offer solutions to these drawbacks. These sensors can take measurements in real time with the as-is sample, they can be fabricated cheaply, they can be portable with low power requirements, and they can be readily integrated into electronic circuitry without direct visual (line of sight) observation needed to obtain the readout. Carbon nanotubes are particularly well suited for use in chemiresistors[10] as they are highly sensitive to changes in their electronic environments[11] and do not require high operating temperatures.[12]

Although non-functionalized single-walled carbon nanotubes (SWCNTs) are known to detect amines chemiresistively,[13] we aimed to improve their sensitivity and specificity to amines through functionalization. SWCNTs can be functionalized covalently or noncovalently with other molecules to impart sensitivity or selectivity for a desired analyte.[14] In particular, noncovalent functionalization allows for facile functionalization without disruption of the electronic properties of the CNTs that can accompany covalent functionalization.[15]

Porphyrins are an attractive platform for functionalizing SWCNTs because their aromatic core is capable of noncovalently binding to the walls of the SWCNTs through the π system.[16] To detect amines, we functionalized SWCNTs with cobalt porphyrins, which are known to bind to amines,[17] can be tuned rationally, and offer an opportunity to examine the effects of oxidation state in amine sensing as both the Co^{II} and Co^{III} species are accessible.

We hypothesized that sensitivity to amines would benefit from increasing the electrophilicity of the Co center by using a relatively electron-withdrawing porphyrin, a weakly coordinating counteranion, and a high oxidation state. Therefore, we synthesized a series of Co porphyrins (Figure 1) allowing for a comparison between *meso*-tetraphenylporphyrinato (tpp) and the more electron-withdrawing *meso*-tetrakis-(pentafluorophenyl)porphyrinato (tpfpp) ligand, between

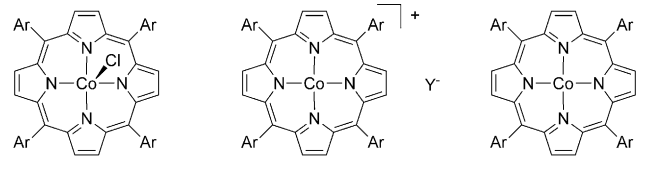

Figure 1. Structures of cobalt porphyrins employed in detectors in this study. Axial aquo ligands are omitted for clarity.

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Cl^- and the more weakly coordinating ClO_4^- and BF_4^- counteranions, and between Co^{III} and the more electron-rich Co^{II} center.

Devices were fabricated by drop-casting a suspension of SWCNTs and the desired porphyrin complex between gold electrodes (1 mm gap) in a 14-channel array with a shared counter electrode, a design we used previously[18] for simultaneous measurement with different composites. We calibrated the responses to various concentrations of NH_3 gas. Low concentrations of NH_3 diluted in N_2 were delivered to the device while a potentiostat applied 0.100 V across the electrodes and recorded the current. A negative change in current resulting from exposure to NH_3 was divided by the initial current to give the change in conductance ($-\Delta G/G_0$), which was taken as the response.

Figure 2a shows the average responses for two devices of each of the materials to three 30 s exposures to NH_3. The responses are approximately linear below 10 ppm, above which they appear to saturate. The responses change from irreversible to semireversible around this concentration as seen in Figure 2b, which shows the baseline-corrected conductance traces of a $[Co(tpfpp)]ClO_4$-based device responding to NH_3. The limit of detection is less than 0.5 ppm NH_3, the lowest concentration that we can reliably deliver with our system. The sensitivity of these porphyrin–SWCNT composites toward NH_3 is more than an order of magnitude greater than that measured for pristine SWCNTs.

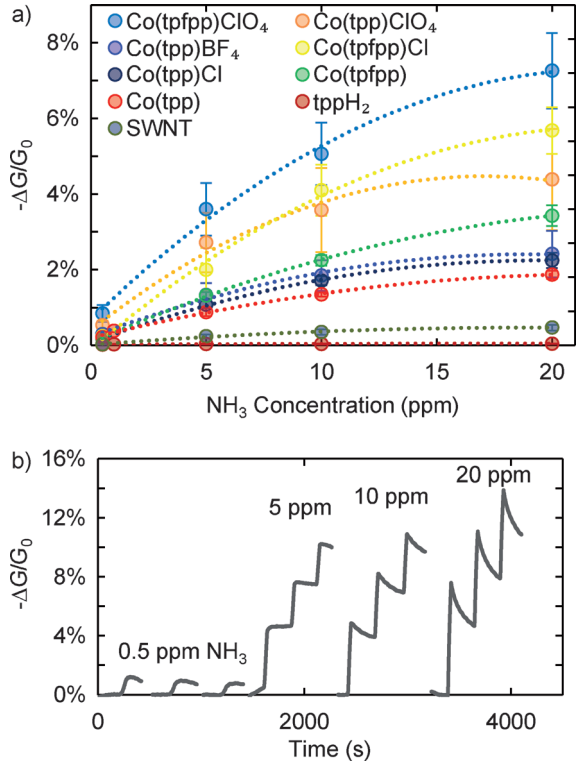

Figure 2. a) Conductance changes of detectors fabricated from porphyrin–SWCNT composites in response to 30 s exposures of various concentrations of NH_3 in N_2 (quadratic fit). b) Conductance traces of a $[Co(tpfpp)]ClO_4$–SWCNT chemiresistor to three 30 s exposures of various concentrations of NH_3 in N_2.

We hypothesized that sensitivity to amines would improve with increased electron deficiency at the Co center. Using the first reduction potential of the complexes as a proxy for electron deficiency, we investigated the correlation between sensitivity to NH_3 and electron deficiency at the Co center. Figure 3 shows the response of the Co composites to 20 ppm

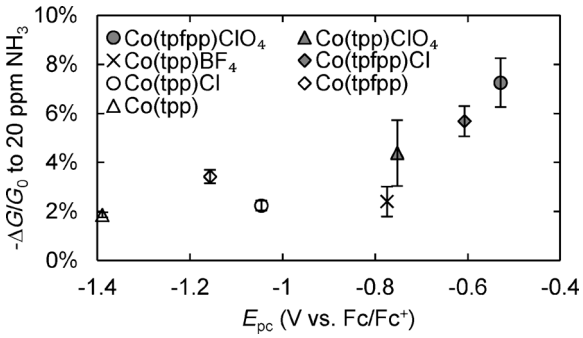

Figure 3. Responses of detectors fabricated from SWCNT/Co-porphyrin composites to 30 s exposures of 20 ppm NH_3 against reduction potentials (potential of first peak cathodic current as measured by cyclic voltammetry of the compounds in PhCN solution vs. Fc/Fc^+).

NH_3 against the first reduction potential of the Co complex. These results suggest that efficacy of this system for NH_3 detection improves with increasing electron deficiency at the metal center.

For monitoring meat spoilage, the detection of BAs, such as putrescine and cadaverine, is pertinent. Figure 4 shows the responses of $[Co(tpfpp)]ClO_4$–SWCNT chemiresistors to exposures to both putrescine (Figure 4a) and cadaverine (Figure 4b). The strong responses are dosimetric and could find utility in single-use wireless tags.[19]

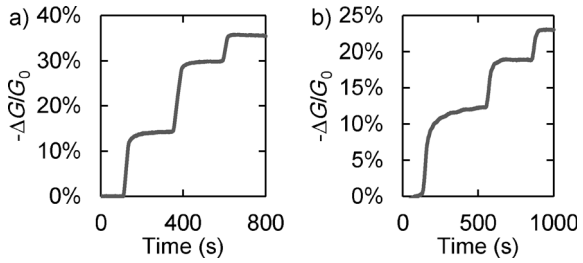

Figure 4. Conductance traces of a $[Co(tpfpp)]ClO_4$–SWCNT chemiresistor to three 30 s exposures of 2.5 ppm of a) putrescine and b) cadaverine.

Detection of BAs in meat samples requires a strategy for distinguishing them from the complex matrix. To assess their selectivity toward amines, we measured responses of $[Co(tpp)]ClO_4$–SWCNT devices to volatile compounds with a wide range of functional groups (Figure 5). The devices exhibit high selectivity for NH_3 among the analytes tested. Species capable of simply coordinating to the Co^{III} center (e.g., H_2O, EtOH, THF, CO) do not elicit a strong response, suggesting that charge transfer is a large component of signal

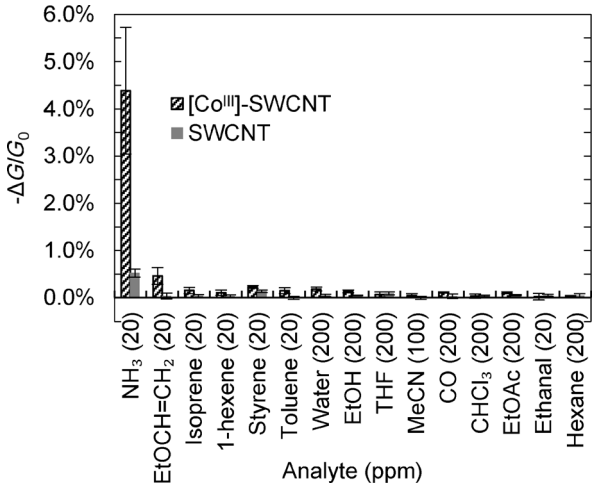

Figure 5. Responses of [Co(tpp)]ClO_4–SWCNT and non-functionalized SWCNT chemiresistors to 30 s exposures of the vapors of various compounds (with concentration in ppm given in parentheses) in N_2.

transduction for amines in this system.[11,13] While the devices alone cannot distinguish amines from each other, their response will reflect the TVBN level with minor contribution from interferents.

We used our detector to compare TVBN emission from day to day for 1.0 g aliquots of various types of raw meat: pork, chicken, salmon, and cod. A sample was placed in a gas flow chamber that we described previously for fruit.[20] N_2 ($0.25\ L\ min^{-1}$) was passed alternately over the detector or first through the chamber holding the meat sample at 25 °C before passing over the detector. The initial peak response at the end of a 30 s exposure was not as reproducible as the ΔG values taken 60 s after the end of the exposure (Figure 6a). This effect may be the result of unknown interfering analytes that give a reversible sensor response. As shown in Figure 4, target BAs are likely to give irreversible responses over time periods reflected in this scheme. Thus, the delay gives a more faithful measurement of these key BAs.

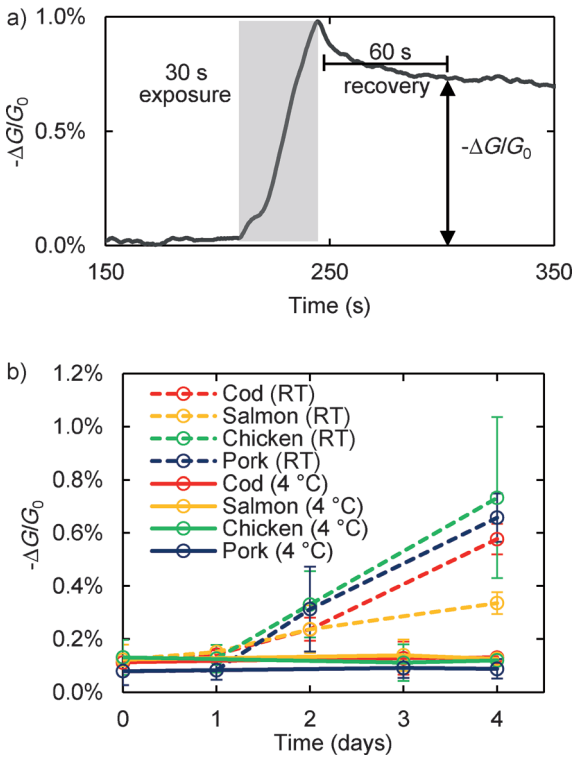

Figure 6. a) Conductance trace of [Co(tpp)]ClO_4–SWCNT chemiresistor during 30 s exposure to vapors from pork (1.0 g) after storage at 22 °C for 4 days. b) Responses of device to 30 s exposures of vapors from various meat samples (1.0 g) stored at 22 °C (RT) or 4 °C for 0–4 days.

The results of the meat-monitoring measurements made with the same [Co(tpp)]ClO_4-based device across 4 days are shown in Figure 6b. Two samples for each meat were monitored, one stored at room temperature (22 °C) and one at 4 °C. For samples stored at 4 °C, the detector showed no increase in response over 4 days. The absence of detectable spoilage for meat samples stored for 4 days at 4 °C is consistent with the literature.[4a] For samples stored at 22 °C, an increase in response was detected after day 1, and even greater responses were recorded by day 4; this increase in TVBN content between days 1 and 2 and the further increase after day 2 is consistent with literature reports for BA levels in meat determined using other techniques (electrochemistry, chromatography,[21] and spectrometry[4a]).

In summary, we developed a chemiresistive detector for amines fabricated from Co porphyrin/SWCNT composites. We demonstrated that rationally tuning the Co oxidation state, the ligand, and the primary coordination sphere of the complex can lead to improvements in sensitivity toward amines, which are detected rapidly at sub-ppm concentrations and with high selectivity. We further showed that the devices can be used to monitor meat spoilage by detecting volatile BAs. The system is an inexpensive, portable method for following the decomposition of various types of meat.

Keywords: amines · cobalt · carbon nanotubes · porphyrinoids · sensors

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