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

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

Sophie F. Liu, Alexander R. Petty, Graham T. Sazama, and Timothy M. Swager*

Abstract: Chemiresistive detectors for amine vapors were made from single-walled carbon nanotubes by non-covalent modification with cobalt meso-arylporphyrin complexes. We show that through changes in the metal’s oxidation state, the electron-withdrawing character of the porphyrin ligand, and the counteranion, the magnitude of 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 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. A detector for meat spoilage could prevent the consumption of unsafe meat or unnecessary discard. One of the most salient markers of meat decomposition is 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 and by amination of carboxyls.

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, spectrometry, electrochemistry, colorimetry, mass balance, chemiluminescence, and electrochemistry. However, these all suffer from one or more drawbacks: extensive sample preparation prior to analysis; expensive, cumbersome instruments with high power consumption; highly trained personnel to operate; and line of sight required to read output.

Electronic sensors such as chemiresistors offer solutions to these drawbacks. They 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 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 as they are highly sensitive to changes in their electronic environments and do not require high operating temperatures.

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

Porphyrrins are an attractive platform for functionalizing SWCNTs because their aromatic core is capable of non-covalently binding to the walls of the SWCNTs with the π system. To detect amines, we functionalized SWCNTs with cobalt porphyrins, which are known to bind to amines, can be tuned rationally, and offer an opportunity to examine the effects of oxidation state in amine sensing as both CoIII and CoII species are accessible.

![Figure 1. Structures of cobalt porphyrins employed in detectors in this study. Axial aquo ligands are omitted for clarity.](image)

We hypothesized that sensitivity to amines would benefit from increasing 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 comparison between meso-tetraphenylporphyrinato (tpp) and the more electron-withdrawing mesotetrakis(pentafluorophenyl)porphyrinato (tpfpp) ligand, between Cl and the more weakly coordinating ClO4 and BF4 counteranions, and between CoIII and more electron-rich CoII.

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 for simultaneous measurement with different composites. We calibrated the responses to various concentrations of NH3. Low concentrations of NH3 diluted in N2 were delivered to the device while a potentiostat applied 0.100 V across the electrodes and recorded current. Negative change in current resulting from exposure to NH3 was divided by initial current to give change in conductance (ΔG/G0), which was taken as the response.

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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$_3$. 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, at which they appear to saturate. The responses change from irreversible to semi-reversible 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 toward NH$_3$ is more than an order of magnitude greater than that of pristine SWCNTs.

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 NH$_3$ against the first reduction potential of the Co complex. These results suggest that efficacy for NH$_3$ detection in this system improves with increasing electron deficiency at the metal center.

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(tppp)]ClO$_4$-SWCNT devices to volatile compounds representing 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$^{3+}$ center (e.g., H$_2$O, EIOH, THF, CO) do not elicit a strong response, suggesting that charge transfer is a large component of signal transduction for amines in this system. 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. N$_2$ (0.25 L/min) 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 $\Delta G$ values taken 60 s after exposure.
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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. Hence, the delay gives a more faithful measurement of
these key BAs.

The results of the meat monitoring measurements made with
the same [Co(tpp)]ClO₄-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 observable spoilage for
meat samples stored for 4 days at 4 °C is consistent with the
literature.[46] For samples stored at 22 °C, an increase in
response was observed after day 1, and even greater responses
were recorded by day 4; this increase in TVBN content between
days 1 and 2 and further increase after day 2 is consistent with
literature reports for BA levels in meat determined using other
techniques (electrochemistry, chromatography,[21] and
spectrometry).[46]

In summary, we developed a chemiresistive detector for
amines fabricated from Co porphyrin/SWCNT composites. We
demonstrated that rationally tuning the Co oxidation state, ligand,
and 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 for
spoilage by detecting volatile BAs. The system represents an
inexpensive, portable method for following the decomposition of
various types of meat.

Keywords: amines • cobalt • nanotubes • porphyrinoids •
sensors

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