Selective Detection of Vapor Phase Hydrogen Peroxide with Phthalocyanine Chemiresistors

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Vapor phase monitoring of peroxides is a topic of critical importance; recent incidents in England and Germany involving peroxide based explosives have made peroxide detection crucial to counterterrorism efforts.[1] Due to its widespread use and toxicity (OSHA PEL = 1 ppm), vapor phase monitoring of hydrogen peroxide (H_2O_2) is also an important industrial health issue.[2] Standard methods of H_2O_2 detection are limited to solid and liquid samples.[3] Therefore, there is an urgent need for rapid vapor phase detection of H_2O_2 with a simple electronic sensor.

Phthalocyanines, both metalated (MPcs; M = p-, d-, and f-block elements) and metal-free (H_2Pc), are organic p-type semiconductors that are used as chemiresistive gas sensors.[4] MPc conductivities are increased by oxidant gases that generate charge carriers (holes) and are decreased by electron-donating gases which trap charge carriers.[5-6] MPcs act as catalysts for solution phase electrochemical oxidation and reduction of H_2O_2;[7] however, MPcs have not been explored as vapor phase H_2O_2 sensors.

Chemiresistors using 50 nm thick films of MPcs (M = Co, Ni, Cu, and H_2) are examined as sensors for vapor phase H_2O_2 detection under practical conditions (i.e., in the presence of ambient humidity). Selectivity is gained from the ability of H_2O_2 to cause current losses in CoPc sensors and current gains in NiPc, CuPc, and H_2Pc sensors; this is the first example of contrasting analyte redox behavior dependent on the MPc metal center in a chemiresistor. The sensors were fabricated and tested as reported previously.[6] Mass flow controllers were combined with impinger flasks to introduce known concentrations of H_2O_2 from a 27.1% ± 2.0% H_2O_2(aq) solution into the testing chamber.[8]

Sensor responses were recorded as time-dependent current plots at constant voltage and temperature (8 V, 50 ± 0.1 °C). There are two temporal components to sensor response and recovery, a fast adsorption/desorption process followed by a slow saturation/desaturation of analyte on the sensing surface.[6] The fast (kinetic) component of the response has been attributed to binding of analyte at oxygen-free metal sites, and the slow (saturation) component, to competitive displacement of bound oxygen. At room temperature, the crossover point between the fast and slow components occurs near 5 min. To probe both temporal components, sensors were dosed with identical concentrations of 27% H_2O_2(aq) in both the kinetic regime (5 min doses with 90 min recoveries) and the saturation regime (30 min doses with 90 min recoveries). The doses consisted of 45 ppm of H_2O_2 accompanied by 4950 ppm of water (relative humidity RH = 17%). In parallel experiments, the sensors were dosed at constant humidity (RH = 17%) in order to distinguish the sensor response of H_2O_2 from that of water. These data are given in Figure 1.

CoPc responds with current losses to each dose of H_2O_2, with or without constant humidity, in both the kinetic and saturation regimes. Conversely, NiPc, CuPc, and H_2Pc respond to H_2O_2 with current gains in the presence or absence of constant humidity. In
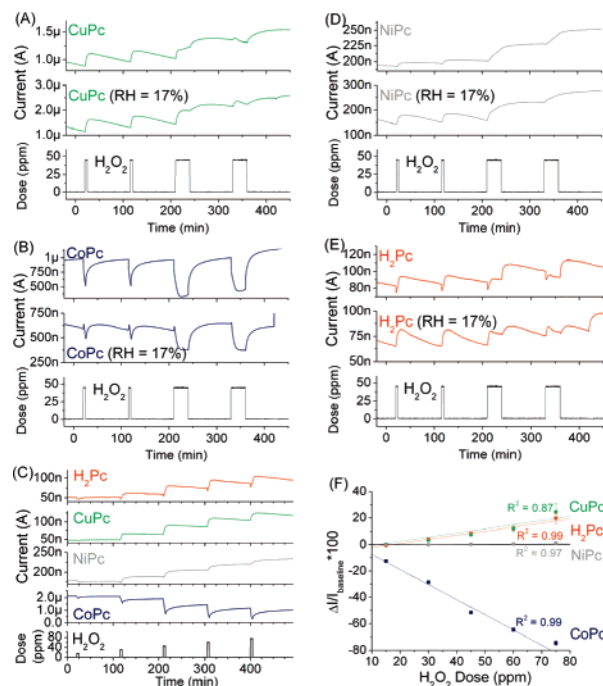

Figure 1. (A) CuPc (green traces) sensing data (50 °C, 8 V) on exposure to 27% H_2O_2(aq) doses (black trace) in the presence and absence of constant humidity. RH = relative humidity. (B) CoPc (blue traces) sensing data. (C) Sensing data for MPcs (M = Co, Ni, Cu, H_2) exposed to varied concentration doses of 27% H_2O_2(aq). (D) NiPc (gray traces) sensing data. (E) H_2Pc (red traces) sensing data. (F) Quantitative sensor response data plotted for each dose in (C).

the saturation regime, all sensors reach a maximum response within 10 min. MPc sensors generally exhibit current losses on exposure to water vapor.[5-6] The NiPc, CuPc, and H_2Pc responses to 27% H_2O_2(aq) are therefore consistent with competing redox effects of H_2O_2 oxidizing the film and water reducing the film. The H_2O_2–MPc film interaction is dominant even in the presence of a concentration of water 100 times greater than H_2O_2. Strong oxidants cause current gains in all CoPc, NiPc, CuPc, and H_2Pc films, while electron donors cause current losses in these same films; H_2O_2 is unique in showing current losses for CoPc and current gains in other MPc films. This is illustrated in Figure 2, which displays sensor responses of CoPc, CuPc, and H_2Pc to selected electron donors[6] and to H_2O_2. Thus a CoPc sensor could be paired with a CuPc/H_2Pc sensor for a peroxide-specific array.

Sensor responses of MPcs exhibit first-order kinetics and therefore are linear with analyte concentration for physisorption and chemisorption interactions.[9] H_2O_2 adsorption kinetics were analyzed by varying the dose concentration (15, 30, 45, 60, and 75 ppm H_2O_2, Figure 1C). Quantitative sensor responses (Figure 1F,
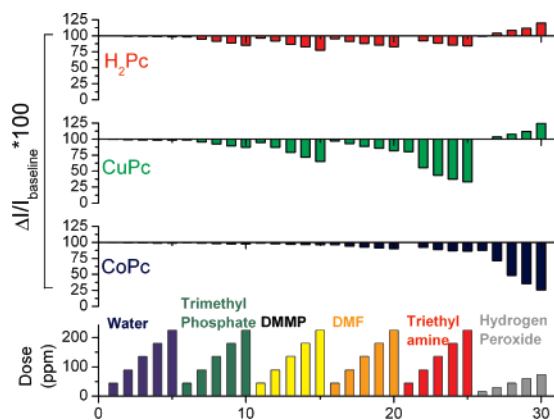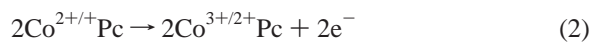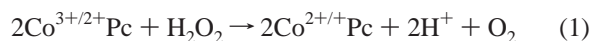
Figure 2. Sensor responses ($\Delta I/I_{baseline}$ * 100) for CoPc (blue), CuPc (green), and H$_2$Pc (red) exposed to various electron donors and H$_2$O$_2$.

Table 1. MPc Sensitivities to H$_2$O$_2$ and Estimated Detection Limits

MPc	H$_2$O$_2$ sensitivity (% ppm^{-1}) × 10^{-2}	H$_2$O$_2$ detection limit (ppm)
CoPc	−103.2 ± 3.3	0.05
NiPc	2.3 ± 0.9	40.1
CuPc	31.2 ± 8.3	12.2
H$_2$Pc	27.6 ± 5.2	11.7

$\Delta I/I_{baseline}$ * 100) for CoPc, NiPc, CuPc, and H$_2$Pc in the kinetic regime are linear with concentration. MPc sensitivities to H$_2$O$_2$ are defined as the slope (% ppm^{-1}) of the sensor response versus dose concentration (Figure 1F, Table 1). Conversely, in the saturation regime, the sensor responses are not linear with H$_2$O$_2$ concentration; instead, the responses depend on dosing history (Figure S1). This unusual behavior is consistent with a chemical or electrochemical reaction modifying the sensor film, rather than simple physisorption or chemisorption.

CoPc is a potent catalyst for H$_2$O$_2$ oxidation and reduction, and the mechanism of H$_2$O$_2$ decomposition in solution has been previously explored.[10] It is inferred from the large current losses observed for CoPc in Figure 1C that cobalt-catalyzed oxidation of H$_2$O$_2$ on the surface of the CoPc film is occurring (with concurrent film reduction), leading to hole trapping and loss of current. The reaction can be written as follows:[10]

$$2Co^{3+/2+}Pc + H_2O_2 \rightarrow 2Co^{2+/+}Pc + 2H^+ + O_2 \quad (1)$$

$$2Co^{2+/+}Pc \rightarrow 2Co^{3+/2+}Pc + 2e^- \quad (2)$$

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^- \quad \textit{overall reaction} \quad (3)$$

In contrast, voltammetric studies of MPcs with nonredox-active metal centers (M = Ni, Cu, and H$_2$) revealed no electrocatalytic behavior in the presence of H$_2$O$_2$,[11] but EPR studies of optically excited ZnPc solutions revealed the presence of $^\bullet$OH radicals, suggesting homolytic cleavage of H$_2$O$_2$.[12] The presence of small amounts of hydroxyl radicals generated during dosing may account for the partial oxidation of NiPc, CuPc, and H$_2$Pc films, leading to the observed sensor responses as radical reactions (eq 4) or as charge-transfer processes (eq 5):[12]

$$MPc + HOOH \rightarrow MPc^{\bullet+} + OH^- + {}^\bullet OH \quad (4)$$

$$MPc + HOOH \rightarrow [MPc - HOOH \rightarrow$$
$$MPc^{\delta+} - HOOH^{\delta-}] \quad (5)$$

MPc chemiresistive sensors offer advantages over existing commercial vapor phase H$_2$O$_2$ detection methods, which suffer from

drawbacks such as cross-reactive interferents and complex instrumentation.[13] Detection limits of the cited commercial H$_2$O$_2$ sensors range from 0.1 to 1 ppm. Detection limits for the chemiresistive MPc sensors examined in this study were calculated from the MPc sensitivities (Table 1) at a signal-to-noise ratio of 3. Due to its high catalytic activity, CoPc is the most sensitive material for detecting H$_2$O$_2$, with a detection limit of 50 ppb. These limits may be further improved by incorporation of a preconcentrator or an ultrathin ChemFET geometry.[14] Detection of peroxide-based explosives (TATP, HMTD) may be achieved by liberation of H$_2$O$_2$ from these explosives by UV light,[3] followed by detection with the MPc sensor array.

In summary we have shown that H$_2$O$_2$ vapors may be selectively detected by contrasting oxidation/reduction behavior in nanoscale chemiresistive films of MPcs. This study presents the first example of MPc vapor sensors showing contrasting current responses to the same analyte based on the specific metal center, which may be attributed to electrocatalytic processes occurring in the sensor film. Therefore, differential response analysis can be used to selectively identify the presence of H$_2$O$_2$ through the combination of only two sensors (e.g., CoPc and CuPc) with opposite sensor responses (Figure 2). This study represents a new approach to selective analyte detection: catalytic redox contrast in a sensor array.

Supporting Information Available: Fabrication and experimental techniques and saturation regime data (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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