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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.

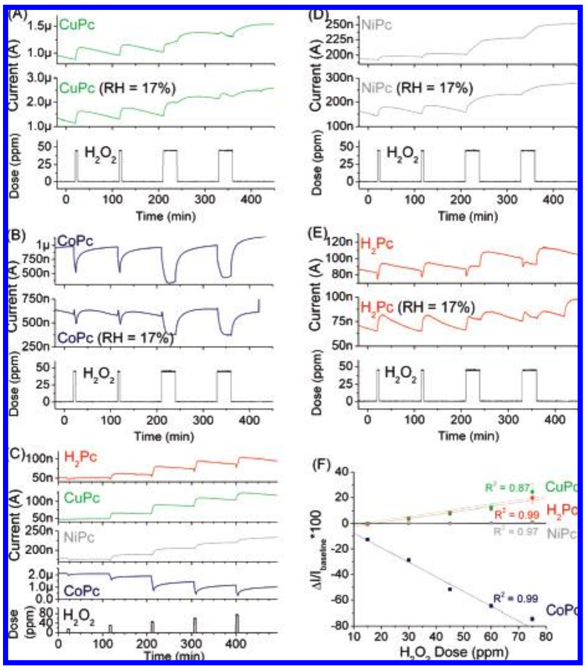

Figure 1. (A) CuPc (green traces) sensing data (50 °C, 8 V) on exposure to 27% H_2O_2(aq) doses (black trace) in the presence and absence of constant humidity. RH = relative humidity. (B) CoPc (blue traces) sensing data. (C) Sensing data for MPcs (M = Co, Ni, Cu, H_2) exposed to varied concentration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

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 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,

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