CHAPTER 1

Introduction

I. OVERVIEW

A. Mammalian vs. Electronic Olfaction

One of most significant parallels between most electronic nose designs and mammalian olfaction is the reliance on a large number of cross-reactive detectors or receptors. In an electronic nose array, the relative response signals of the individual detector elements, often termed the 'response pattern,' provide the array with its identification, discrimination, and classification capabilities. This cross-reactive design [1], as opposed to a 'lock and key' approach in which an individual detector is intended to interact selectively with only a single analyte, is fundamentally similar to the evolutionarily derived organization of mammalian olfaction, which also relies primarily on cross-reactive receptors [2] to provide a response pattern to the olfactory cortex [3-5]. In mammals, the number of these functionally distinct receptors is estimated be on the order of 10^3 [2], while in most electronic nose systems studied to date, the number of chemically unique detectors is typically much smaller [1]. Although electronic nose technologies have made progress in a range of tasks, such as in locating explosives [6-8] and in the detection of disease biomarkers [9, 10], in many ways the olfactory systems of mammals, and particularly those of canines [11, 12], are still superior. One of the reasons for this, is that the mammalian olfactory system has also evolved to use many other tricks for odorant detection and identification beyond simply the diversity of its array of 'cross-reactive' receptors [12-14]. Clearly, there are still many lessons in biological olfactory systems that can be applied to the design of electronic nose systems. This practice of applying principles from the natural world to the development of a man-made system is often referred to as bio-inspired design, and some examples of this bio-inspired design will be evident in this thesis.

B. Sensor Technologies

Several early electronic noses were based on resistance (or the effective resistance) measurements of semiconductor devices such as tin-oxide gas sensors [28] and MOSFET gas sensors [29]. These technologies both rely on specific reactions between the gas and the semiconductor or the gate electrode. A new type of chemically sensitive resistor sensor is described in Chapter 2, which uses alkylamine-capped gold nanocrystals as a composite material. These detectors, which are in some ways like the 'lock and key' type sensors described above, also rely on specific reactions between the analyte gas and the senor material, and exhibit some new properties and gas sensitivities that are not observed in other chemically sensitive resistors, but that are evident in trends of mammalian olfactory sensitivities.

A different category of sensor that has gained significant recent attention uses 'sorption-based' detectors. These detectors exploit the equilibrium sorption of an analyte vapor into an organic phase as the initial step in detection of the vapor. Some examples of detectors in this group are carbon black-polymer composites [15], conducting organic polymers [16-19], polymer-coated quartz crystal microbalances (QCM) [20], polymer-coated surface acoustic wave devices (SAW) [21, 22], polymer-coated capacitors [23], and arrays of dye-impregnated polymeric beads or coated optical fibers [24-26]. The magnitude of the steady-state response of such sorption-based detectors depends primarily on the equilibrium partition coefficient of the analyte into the polymer [27].

Chapters 3 and 4 of this thesis focus on carbon black-polymer composite chemically sensitive resistors based on the sorption of an analyte into a polymer film. These sensors are formed by the dispersion of electrically conductive carbon black into a matrix of insulating organic polymers [15, 18, 30]. Arrays of this type are cross-reactive, meaning that a given analyte molecule produces a signal on more than one detector, and a given detector produces a signal for more than one analyte. Carbon black conductor,

which comes from the high temperature furnace combustion of a petroleum feedstock, is mixed with an insulating polymer at a volume fraction sufficient to exceed the percolation threshold of the composite [31-34]. When the volume fraction of the conductor is above the percolation threshold, a network of conductive pathways will extend completely through the insulating film, instilling the electrical conductivity necessary for resistance measurements. The insulating polymer fraction of the composite provides an easily variable source of chemical diversity necessary for fabricating a differentially responsive array.

Percolation theory has been shown to describe the resistivity, ρ, of carbon black-insulating polymer composites as a function of the resistivities of the carbon black, ρ_{cb}, and the insulating polymer, ρ_{ip}, and can be written as

$$\rho = \frac{(z-2)\rho_{cb}\rho_{ip}}{A+B+[(A+B)^2+2(z-2)\rho_{cb}\rho_{ip}]^{1/2}} \tag{1a}$$

where

$$A = \rho_{cb}\left[-1+(z/2)(1-(v_{cb}/f))\right] \tag{1b}$$

$$B = \rho_{ip}[(zv_{cb}/2f)-1] \tag{1c}$$

and where z is the coordination number of the conductive particle, v_{cb} is the volume fraction of the carbon black, and f is the total packing fraction. Thus the swelling of the composite films during the sorption process [35], via incorporation of a volume of analyte vapor, produces a positive dc electrical resistance change, which is consistent with percolation theory assuming an increased total volume of the insulator. Simple spin and spray-coating deposition techniques permit the fabrication of such chemiresistor-type vapor detectors in a wide range of geometries and film thicknesses and on virtually any substrate that provides two electrical contacts to the film.

Much of the previous work on vapor sensing arrays has focused on the chemical differences between the different detector elements as the source of the identification and classification information of the array. This is similar to the concept of structurally different receptors in mammalian olfaction; however, as mentioned above, mammals are also believed to use additional clues such as spatiotemporal information for processing odor signals [13, 36, 37]. Chapters 3 and 4 will demonstrate improved performance of carbon black-polymer arrays by using this spatial and temporal information. These chapters will also address some of the fundamental properties of carbon black-polymer composite sensors and provide indications of how to optimize arrays of these detectors for a given task.

II. ORGANIZATION OF THESIS

This dissertation explores new principles of vapor detection based on chemically sensitive resistors. The work is divided into three separate chapters which appear in the chronological order that the research was carried out. Chapter 2 describes a new type of vapor sensor based on alkylamine-capped gold nanocrystals, that is both highly sensitive and highly selective for small mercaptan vapors and gases. Chapter 3 explores the geometrical factors influencing the signal/noise properties of carbon black-polymer composite vapor sensors and also demonstrates a new design principle for separating and targeting analyte onto detectors optimized to provide the best signal/noise ratio for that analyte [38]. Although my advisor, Prof. Lewis, contributed in immeasurable ways to the work described in all of the chapters in this thesis, the work in Chapter 3 also includes notable efforts from two additional people, Dr. Phil Tokumaru and Dr. Michael S. Freund. Dr. Tokumaru contributed both to the theoretical section and to the design of one of the substrates, and Dr. Freund helped in the analysis of the experiments. Chapter 4 explores the time response of polymer-carbon black composite vapor sensors in response to well-defined short rise-time vapor pulses. A simple model for the sensor time response based on Fickian diffusion is developed and compared with the experimental data.

III. REFERENCES

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