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A chemically diverse conducting polymer-based "electronic nose"

[sensor arrays/olfaction/principal component analysis/poly(pyrrole)/plasticizers]

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ABSTRACT **We describe a method for generating a variety of chemically diverse broadly responsive low-power vapor sensors. The chemical polymerization of pyrrole in the presence of plasticizers has yielded conducting organic polymer films whose resistivities are sensitive to the identity and concentration of various vapors in air. An array of such sensing elements produced a chemically reversible diagnostic pattern of electrical resistance changes upon exposure to different odorants. Principal component analysis has demonstrated that such sensors can identify and quantify different airborne organic solvents and can yield information on the components of gas mixtures.**

There is considerable interest in developing sensors that act as analogs of the mammalian olfactory system (1, 2). This system is thought to utilize probabilistic repertoires of many different receptors to recognize a single odorant (3, 4). In such a configuration, the burden of recognition is not on highly specific receptors, as in the traditional "lock-and-key" molecular recognition approach to chemical sensing, but lies instead on the distributed pattern processing of the olfactory bulb and the brain (5, 6). We describe herein the construction and characterization of a broadly responsive vapor detection array based on conducting polymer "chemiresistor" elements. Such conducting polymer elements are simply prepared and are readily modified chemically to respond to a broad range of analytes. In addition, these sensors yield a fairly rapid low-power dc electrical signal in response to the vapor of interest, and their signals are readily integrated with software- or hardware-based neural networks for purposes of analyte identification.

Prior attempts to produce a broadly responsive sensor array have exploited heated metal oxide thin film resistors (7–9), polymer sorption layers on the surfaces of acoustic wave resonators (10, 11), arrays of electrochemical detectors (12–14), or conductive polymers (15, 16). Arrays of metal oxide thin film resistors, typically based on SnO_2 films that have been coated with various catalysts, yield distinct diagnostic responses for several vapors (7–9). However, due to the lack of understanding of catalyst function, SnO_2 arrays do not allow deliberate chemical control of the response of elements in the arrays nor reproducibility of response from array to array. Surface acoustic wave resonators are extremely sensitive to both mass and acoustic impedance changes of the coatings in array elements, but the signal transduction mechanism involves somewhat complicated electronics, requiring frequency measurement to 1 Hz while sustaining a 100-MHz Rayleigh wave in the crystal (10, 11). Electrically conductive organic polymer elements are well-suited for such an array, because swelling of the polymer upon exposure to an analyte will induce changes in the resistivity of the polymer film (17, 18). This enables a direct low-power electrical signal readout (the film resistance) to be used as the sensing signal. Some prior work has been performed with conducting polymer elements that have been grown electrochemically, with the variation in each element being obtained through nominally identical polymer films and coatings that possess an incremental, but usually unpredictable, variation in swelling properties in each sensor element (15, 16).

Our approach has been to prepare processable thin films of electrically conducting organic polymers as the individual sensor elements. Use of processable films has allowed deliberate control over the chemical properties of the resulting conducting polymer coatings. Such films can be plasticized during deposition, providing diversity and systematic control over the chemical binding properties of each "chemiresistor" element. Specifically, we have utilized the chemical polymerization of pyrrole under controlled conditions to produce thin conducting films on nonconducting substrates. By using this methodology, we have prepared a variety of polymer films that have distinctly different electrical resistance responses to various vapors and have obtained diagnostic array signal patterns in response to a series of test odorants.

MATERIALS AND METHODS

Polymer Synthesis. Poly(pyrrole) films used for conductivity, electrochemical, and optical measurements were prepared by injecting equal volumes of N_2-purged solutions of pyrrole (1.50 mmol in 4.0 ml of dry tetrahydrofuran) and phosphomolybdic acid (0.75 mmol in 4.0 ml of tetrahydrofuran) into a N_2-purged test tube. Once the two solutions were mixed, the yellow phosphomolybdic acid solution turned dark green, with no observable precipitation for several hours. This solution was used for film preparation within an hour of mixing.

Sensor Fabrication. Plasticized poly(pyrrole) sensors were made by mixing two solutions: one solution contained 0.29 mmol of pyrrole in 5.0 ml of tetrahydrofuran and the other solution contained 0.25 mmol of phosphomolybdic acid and 30 mg of plasticizer in 5.0 ml of tetrahydrofuran. The mixture of these two solutions resulted in a pyrrole/plasticizer ratio of 2:3 (wt/wt). An inexpensive quick method for creating the chemiresistor array elements was accomplished by effecting a cross-sectional cut through commercial 22-nF ceramic capacitors (Kemet Electronics, Greenville, SC). Mechanical slices through these capacitors revealed a series of interdigitated metal lines (25% Ag/75% Pd), separated by 15 μm, that could be readily coated with conducting polymer. The monomer/plasticizer/oxidant solutions were then used to dip-coat interdigitated electrodes to provide a robust electrical contact to the polymerized organic films. After polymerization was complete, the film was insoluble and was rinsed with solvent (tetrahydrofuran or methanol) to remove residual phosphomolybdic acid and unreacted monomer. The sensors were then connected to a commercial bus strip, with the resistances of the various chemiresistor elements readily monitored by use of a multiplexing digital ohmmeter.

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Principal Component Analysis and Multilinear Least Squares Fits. A data set obtained from a single exposure of the array to an odorant produced a set of descriptors (i.e., resistances), d_i. The data obtained from multiple exposures thus produced a data matrix **D**, where each row, designated by j, consisted of n descriptors describing a single member of the data set (i.e., a single exposure to an odor). Since the baseline resistance and the relative changes in resistance varied among sensors, the data matrix was autoscaled before further processing (19). In this preprocessing technique, all the data associated with a single descriptor (i.e., a column in the data matrix) were centered around zero with unit standard deviation

$$d'_{ij} = (d_{ij} - \bar{d}_i)/\sigma_i, \quad [1]$$

where $\bar{d}_i$ is the mean value for descriptor i and σ_i is the corresponding standard deviation.

Principal component analysis (19) was performed to determine linear combinations of the data such that the maximum variance (defined as the square of the standard deviation) between the members of the data set was obtained in n mutually orthogonal dimensions. The linear combinations of the data resulted in the largest variance (or separation) between the members of the data set in the first principal component (pc1) and produced decreasing magnitudes of variance from the second to the nth principal components (pc2–pc$n$). The coefficients required to transform the autoscaled data into principal component space (by linear combination) were determined by multiplying the data matrix **D** by its transpose, $\mathbf{D^T}$ (i.e., diagonalizing the matrix) (19),

$$\mathbf{R} = \mathbf{D^T \cdot D}. \quad [2]$$

This operation produced the correlation matrix **R** whose diagonal elements were unity and whose off-diagonal elements were the correlation coefficients of the data. The total variance in the data was thus given by the sum of the diagonal elements in **R** before autoscaling. The n eigenvalues, and the corresponding n eigenvectors, were then determined for **R.** Each eigenvector contained a set of n coefficients that were used to transform the data by linear combination into one of its n principal components. The corresponding eigenvalue yielded the fraction of the total variance that was contained in that principal component. This operation produced a principal component matrix, **P**, that had the same dimensions as the original data matrix. Under these conditions, each row of the matrix **P** was still associated with a particular odor and each column was associated with a particular principal component.

Since values in the principal component space had no physical meaning, it was useful to express the results of the principal component analysis in terms of physical parameters such as partial pressure and mole fraction. This was achieved via a multilinear least squares fit between the principal component values and the corresponding parameter of interest. A multilinear least squares fit resulted in a linear combination of the principal components that yielded the best fit to the corresponding parameter value. Fits were achieved by appending a column with each entry being unity to the principal component matrix **P**, with each row j corresponding to a different parameter value (e.g., partial pressure) v_j contained in vector **V**. The coefficients for the best multilinear fit between the principal components and parameter of interest were obtained by the matrix operation

$$\mathbf{C} = (\mathbf{P^T \cdot P})^{-1} \cdot \mathbf{P^T \cdot V}, \quad [3]$$

where **C** was a vector containing the coefficients for the linear combination.

RESULTS AND DISCUSSION

A key to our ability to fabricate chemically diverse sensing elements was the preparation of processable air-stable films of electrically conducting organic polymers. This was achieved through the controlled chemical oxidation of pyrrole (PY) with phosphomolybdic acid ($H_3PMo_{12}O_{40}$) (20) in tetrahydrofuran:

$$PY \rightarrow PY^{+\cdot} + e^- \quad [4]$$

$$2PY^{+\cdot} \rightarrow PY_2 + 2H^+ \quad [5]$$

$$H_3PMo_{12}O_{40} + 2e^- + 2H^+ \rightarrow H_5PMo_{12}O_{40} \quad [6]$$

The redox-driven and electrochemically induced polymerization of pyrrole has been explored (21), but this process typically yields insoluble intractable deposits of polypyrrole as the product. Our approach was to use low concentrations of the $H_3PMo_{12}O_{40}$ oxidant (E° = +0.36 V vs. SCE) (20). Since the electrochemical potential of $PY^{+\cdot}/PY$ is more positive (E° = +1.30 V vs. SCE) (22) than that of $H_3PMo_{12}O_{40}/H_5PMo_{12}O_{40}$, the equilibrium concentration of $PY^{+\cdot}$, and thus the rate of polymerization, was relatively low in dilute solutions (0.19 M PY/0.09 M $H_3PMo_{12}O_{40}$). However, it has been shown that the oxidation potential of pyrrole oligomers decreases from +1.20 V to +0.55 V to +0.26 V vs. SCE as the number of units increases from one to two to three and that the oxidation potential of bulk polypyrrole occurs at −0.10 V vs. SCE (23). As a result, oxidation of pyrrole trimers by phosphomolybdic acid is expected to be thermodynamically favorable. This allowed processing of the monomer/oxidant solution (i.e., spin coating, dip coating, introduction of plasticizers, etc.), after which time polymerization to form thin films was simply effected by evaporation of the solvent. The dc electrical conductivity of polypyrrole films formed by this method on glass slides, after rinsing the films with methanol to remove excess phosphomolybdic acid and/or monomer, was on the order of 15–30 S/cm for films ranging from 40 to 100 nm thick.

The polypyrrole films produced in this work exhibited excellent electrochemical and optical properties. For example, the cyclic voltammetric behavior of a chemically polymerized polypyrrole film showed a cathodic wave at −0.40 V, which corresponded to the reduction of polypyrrole to its neutral nonconducting state, and an anodic wave at −0.20 V, which corresponded to the reoxidation of polypyrrole to its conducting state (24). The lack of additional faradaic current, which would result from the oxidation and reduction of phosphomolybdic acid in the film, suggested that the Keggin structure of phosphomolybdic acid was not present in the film (25) and implies that MoO_4^{2-}, or other anions, served as the polypyrrole counterions in the polymerized films. The optical spectra of these films were also in accord with expectations for polypyrrole, with the processed film displaying an absorption band at 4.0 eV (1 eV = 1.602×10^{-19} J) (26, 27).

As described in the experimental section, various plasticizers were introduced into the polymer films (Table 1). This allowed chemical control over the binding properties and electrical conductivity of the resulting plasticized polymers. Sensor arrays consisted of as many as 14 elements, with each element synthesized to produce a distinct chemical composition and, thus, a distinct sensor response for its polymer film. The resistance R of each film-coated individual sensor was automatically recorded before, during, and after exposure to various odorants. A typical trial consisted of a 60-sec rest period in which the sensors were exposed to flowing air (3.0 liters/min), a 60-sec exposure to a mixture of air (3.0 liters/min) and air that had been saturated with solvent (0.5–3.5 liters/min), and then a 240-sec exposure to air (3.0 liters/min).

In an initial processing of the data, presented in this paper, the only information used was the maximum amplitude of the

Table 1. Plasticizers used in array elements

Sensor	Plasticizer
1	None
2	None*
3	Polystyrene
4	Polystyrene
5	Polystyrene
6	Poly(α-methylstyrene)
7	Poly(styrene-*co*-acrylonitrile)
8	Poly(styrene-*co*-maleic anhydride)
9	Poly(styrene-*co*-allyl alcohol)
10	Polyvinylpyrrolidone
11	Poly(vinyl phenol)
12	Poly(vinyl butral)
13	Poly(vinyl acetate)
14	Polycarbonate

Sensors contained a pyrrole/plasticizer ratio of 2:3 (wt/wt).
*Film not rinsed to remove excess phosphomolybdic acid.

resistance change divided by the initial resistance, $\Delta R_{max}/R_i$, of each sensor element. Most of the sensors exhibited either increases or decreases in resistance upon exposure to different vapors, as expected from changes in the polymer properties upon exposure to different types of chemicals (17, 18). However, in some cases, sensors displayed an initial decrease followed by an increase in resistance in response to a test odor. Since the resistance of each sensor could increase and/or decrease relative to its initial value, two values of $\Delta R_{max}/R_i$ were reported for each sensor. The source of the bidirectional behavior of some sensor–odor pairs has not yet been studied in detail, but in most cases this behavior arose from the presence of water (which by itself induced rapid decreases in the film resistance) in the reagent-grade solvents used to generate the test odors of this study. The observed behavior in response to these air-exposed water-containing test solvents was reproducible and reversible on a given sensor array, and the environment was representative of many practical odor sensing applications in which air and water would not be readily excluded.

Fig. 1 *B–D* depicts representative examples of sensor amplitude responses of a sensor array (Table 1). In this experiment, data were recorded for three exposures to vapors of acetone, benzene, and ethanol flowing in air. It is readily apparent that these odorants each produced a distinctive response on the sensor array. In additional experiments, a total of eight vapors (acetone, benzene, chloroform, ethanol, isopropyl alcohol, methanol, tetrahydrofuran, and ethyl acetate), chosen to span a range of chemical and physical characteristics, were evaluated over a 5-day period on a 14-element sensor array (Table 1). As discussed below, each odorant could be clearly and reproducibly identified from the others by using this sensor apparatus.

Principal component analysis (19) was used to simplify presentation of the data and to quantify the distinguishing abilities of individual sensors and of the array as a whole. In this approach, linear combinations of the $\Delta R_{max}/R_i$ data for the elements in the array were constructed such that the maximum variance [defined as the square of the standard deviation] was contained in the fewest mutually orthogonal dimensions. This allowed representation of most of the information contained in data sets shown in Fig. 1 *B–D* in two (or three) dimensions. The resulting clustering, or lack thereof, of like exposure data in the new dimensional space was used as a measure of the distinguishing ability and of the reproducibility of the sensor array.

To illustrate the variation in sensor response of individual sensors that resulted from changes in the plasticizing polymer, principal component analysis was performed on the individual isolated responses of each of the 14 sensor elements in a typical

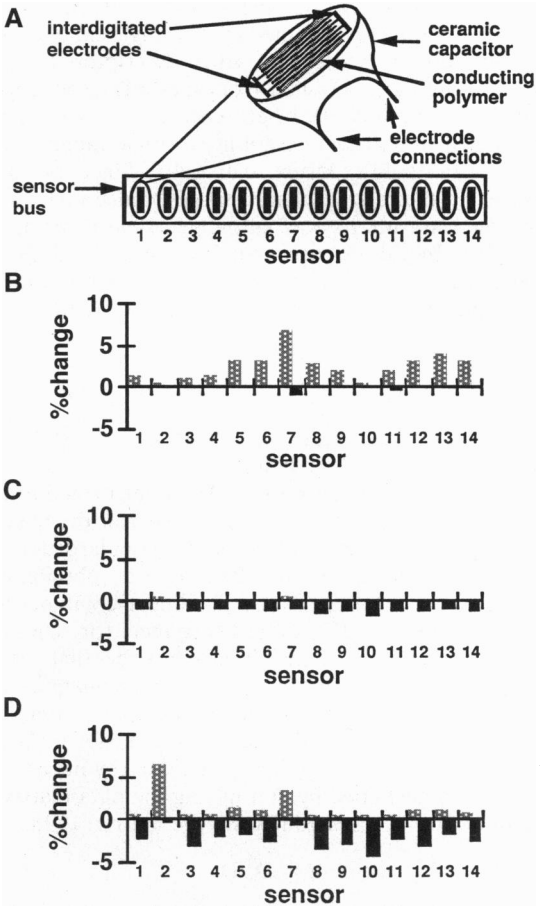

FIG. 1. (*A*) Schematic of a sensor array showing an enlargement of one of the modified ceramic capacitors used as sensing elements. The response patterns generated by the sensor array described in Table 1 are displayed for acetone (*B*), benzene (*C*), and ethanol (*D*). The sensor response was defined as the maximum percent increase and decrease of the resistance divided by the initial resistance (shaded bars and solid bars, respectively) of each sensor upon exposure to solvent vapor. In many cases, sensors exhibited reproducible increases and decreases in resistance. An exposure consisted of (*i*) a 60-sec rest period in which the sensors were exposed to flowing air (3.0 liters/min), (*ii*) a 60-sec exposure to a mixture of air (3.0 liters/min) and air that had been saturated with solvent (0.5 liters/min), and (*iii*) a 240-sec exposure to air (3.0 liters/min).

array (Fig. 2). Since each sensor produced two data values, principal component analysis of these responses resulted in only two orthogonal principal components, pc1 and pc2. As an example of the selectivity exhibited by an individual sensor element, the sensor designated as number 5 in Fig. 2 [which was plasticized with polystyrene] confused acetone with chloroform with isopropyl alcohol and tetrahydrofuran. It also confused benzene with ethyl acetate but easily distinguished ethanol and methanol from all other solvents. Changing the plasticizer to poly(α-methylstyrene) (sensor number 6 in Fig. 2) had little effect on the spatial distribution of the responses with respect to one another and with respect to the origin. Thus, as expected, a rather slight chemical modification of the plasticizer had little effect on the relative variance of the eight test odorants. In contrast, the addition of a cyano group to the plasticizer, in the form of poly(styrene-*co*-acrylonitrile) (sensor number 7 in Fig. 2) resulted in a larger contribution to the overall variance by benzene and chloroform, while decreasing the contribution of ethanol. Changing the substituent group in the plasticizer to a hydrogen bonding acid [poly(styrene-*co*-allyl alcohol), sensor number 9 in Fig. 2] increased the contribution of acetone to the overall variance while having

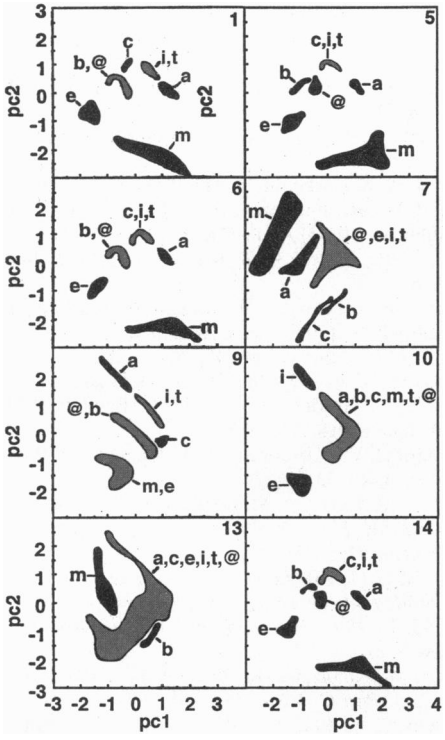

FIG. 2. Principal component analysis of autoscaled data from individual sensors containing different plasticizers. Data were obtained from multiple exposures to acetone (a), benzene (b), chloroform (c), ethanol (e), isopropyl alcohol (i), methanol (m), tetrahydrofuran (t), or ethyl acetate (@) over a period of 5 days with the test vapors exposed to the array in various sequences. The numbers of the figures refer to the sensor elements described in Table 1. The units along the axes indicate the amplitude of the principal component that was used to describe the particular data set for an odor. The solid regions indicate data clusters corresponding to a single solvent that could be distinguished from all others; shaded regions highlight data of solvents whose signals overlapped with others around it. Exposure conditions were identical to those in Fig. 1.

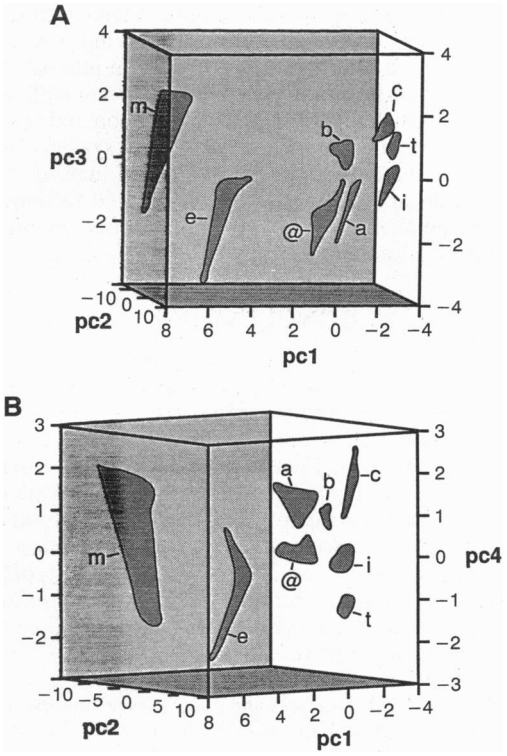

FIG. 3. Principal component analysis of data obtained from all sensors (Table 1). Conditions and symbols are as in Fig. 2. (*A*) Data represented in the first three principal components pc1, pc2, and pc3. (*B*) Data when represented in pc1, pc2, and pc4. A higher degree of discrimination between some solvents could be obtained by considering the fourth principal component as illustrated by larger separations of chloroform, tetrahydrofuran, and isopropyl alcohol in *B*.

little effect on the other odors, with the exception of confusing methanol and ethanol. These results suggest that the behavior of the sensors can be systematically altered by varying the chemical composition of the plasticizing polymer.

Fig. 3 shows the principal component analysis for all of the 14 sensors described in Table 1 and Fig. 1. When the solvents were projected into a three-dimensional odor space (Fig. 3 *A* or *B*), all eight solvents were easily distinguished with the specific array discussed herein. Detection of an individual test odor, based only on the criterion of observing $\approx 1\%$ $\Delta R_{max}/R_i$ values for all elements in the array, was readily accomplished at the parts per thousand level with no control over the temperature or humidity of the flowing air. Further increases in sensitivity are likely after a thorough utilization of the temporal components of the $\Delta R_{max}/R_i$ data as well as a more complete characterization of the noise in the array.

We have also investigated the suitability of this sensor array for identifying the components of certain test mixtures. This task is greatly simplified if the array exhibits a predictable signal response as the concentration of a given odorant is varied and if the responses of various individual odors are additive (i.e., if superposition is maintained). When a 19-element sensor array was exposed to a number, n, of different acetone concentrations in air, the $(CH_3)_2CO$ concentration was semiquantitatively predicted from the first principal component. This was evident from a good linear least squares fit of the partial pressure of acetone, P_a (torr; 1 torr = 133.3 Pa), in air with the first principal component ($P_a = 8.26 \cdot pc1 + 83.4$; $R^2 = 0.989$). The acetone concentration could be more accurately predicted by using a multilinear least squares fit through the first three principal components ($P_a = 8.26 \cdot pc1 - 0.673 \cdot pc2 + 6.25 \cdot pc3 + 8.34$; $R^2 = 0.998$).

The same sensor array was also able to resolve the components in various test methanol/ethanol mixtures (28). A linear relationship was observed between the first principal component and the mole fraction of methanol in the liquid phase, x_m, in a CH_3OH/C_2H_5OH mixture ($x_m = 0.112 \cdot pc1 + 0.524$; $R^2 = 0.979$), demonstrating that superposition held for this mixture/sensor array combination. Furthermore, although the components in the mixture could be predicted fairly accurately from just the first principal component, an increase in the accuracy could be achieved by using a multilinear least squares fit through the first three principal components ($x_m = 0.112 \cdot pc1 - 0.0300 \cdot pc2 - 0.0444 \cdot pc3 + 0.524$; $R^2 = 0.987$). This relationship held for $CH_3OH/(CH_3OH + C_2H_5OH)$ ratios of 0 to 1.0 in air-saturated solutions of this vapor mixture. The conducting polymer-based sensor arrays could, therefore, not only distinguish between pure test vapors but also allowed analysis of concentrations of odorants and analysis of binary mixtures of vapors.

In summary, the results presented herein provide a basis for advances in the area of odor sensor design. A relatively simple array design, using only a multiplexed low-power dc electrical resistance readout signal, has been shown to readily distinguish between various test odorants. Such conducting polymer-based arrays are simple to construct and modify and afford an opportunity to effect chemical control over the response pattern of a vapor. For example, by increasing the ratio of plasticizer to conducting polymer, it should be possible to approach the percolation threshold, at which point the conductivity should exhibit a very sensitive response to the presence of the sorbed molecules. Furthermore, producing thinner

films will afford the opportunity to obtain decreased response times, and increasing the number of plasticizing polymers and polymer backbone motifs will likely result in increased diversity among sensors. This type of chemical control, with its accompanying simplicity of signal transduction and readout, is the main feature of these odor sensors. Such systems also hold potential for evaluating the generality of neural network algorithms that are currently being developed to understand how the mammalian olfactory system identifies the directionality, concentration, and identity of various odors.

CONCLUSIONS

A broadly responsive conducting-polymer-based sensor array has been constructed and has been shown to yield distinctive signal patterns in response to various test odorants. Eight test odorants have been clearly distinguished by using these arrays, with no deliberate control over humidity or temperature of the array elements. This type of polymer-based array is chemically flexible, is simple to fabricate, modify, and analyze, and utilizes a low-power dc resistance readout signal transduction path to convert chemical data into electrical signals. It offers an approach to developing broadly responsive odor sensors for fundamental and applied investigations of chemical mimics for the mammalian sense of smell.

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1. Lundström, I., Erlandsson, R., Frykman, U., Hedborg, E., Spetz, A., Sundgren, H., Welin, S. & Winquist, F. (1991) *Nature (London)* **352,** 47–50.
2. Shurmer, H. V. & Gardner, J. W. (1992) *Sens. Actuators* **8,** 1–11.
3. Reed, R. R. (1992) *Neuron* **8,** 205–209.
4. Lancet, D. & Ben-Arie, N. (1993) *Curr. Biol.* **3,** 668–674.
5. Kauer, J. S. (1991) *Trends Neurosci.* **14,** 79–85.
6. DeVries, S. H. & Baylor, D. S. (1993) *Cell* **10,** 139–149.
7. Gardner, J. W., Shurmer, H. V. & Corcoran, P. (1991) *Sens. Actuators* **4,** 117–121.
8. Gardner, J. W., Shurmer, H. V. & Tan, T. T. (1992) *Sens. Actuators* **6,** 71–75.
9. Corcoran, P., Shurmer, H. V. & Gardner, J. W. (1993) *Sens. Actuators* **15,** 32–37.
10. Grate, J. W. & Abraham, M. H. (1991) *Sens. Actuators* **3,** 85–111.
11. Grate, J. W., Rosepehrsson, S. L., Venezky, D. L., Klusty, M. & Wohltjen, H. (1993) *Anal. Chem.* **65,** 1868–1881.
12. Stetter, J. R., Jurs, P. C. & Rose, S. L. (1986) *Anal. Chem.* **58,** 860–866.
13. Stetter, J. R., Findlay, M. W., Maclay, G. J., Zhang, J., Vaihinger, S. & Gopel, W. (1990) *Sens. Actuators* **1,** 43–47.
14. Stetter, J. R., Findlay, M. W., Schroeder, K. M., Yue, C. & Penrose, W. R. (1993) *Anal. Chim. Acta* **284,** 1–11.
15. Pearce, T. C., Gardner, J. W., Friel, S., Bartlett, P. N. & Blair, N. (1993) *Analyst* **118,** 371–377.
16. Shurmer, H. V., Corcoran, P. & Gardner, J. W. (1991) *Sens. Actuators* **4,** 29–33.
17. Topart, P. & Josowicz, M. (1992) *J. Phys. Chem.* **96,** 7824–7830.
18. Charlesworth, J. M., Partridge, A. C. & Garrard, N. (1993) *J. Phys. Chem.* **97,** 5418–5423.
19. Hecht, H. G. (1990) *Mathematics in Chemistry: An Introduction to Modern Methods* (Prentice Hall, Englewood Cliffs, NJ).
20. Pope, M. T. (1983) *Heteropoly and Isopoly Oxometalates* (Springer, New York).
21. Salmon, M., Kanazawa, K., Diaz, A. F. & Krounbi, M. (1982) *J. Polym. Sci. Part C Polym. Lett.* **20,** 187–193.
22. Andrieux, C. P., Audebert, P., Hapiot, P. & Savéant, J.-M. (1990) *J. Am. Chem. Soc.* **112,** 2439–2440.
23. Diaz, A. F., Crowley, J., Bargon, J., Gardini, G. P. & Torrance, J. B. (1981) *J. Electroanal. Chem.* **121,** 355–361.
24. Kanazawa, K. K., Diaz, A. F., Krounbi, M. T. & Street, G. B. (1981) *Synth. Met.* **4,** 119–130.
25. Bidan, G., Genies, E. M. & Lapkowski, M. (1988) *J. Electroanal. Chem.* **251,** 297–306.
26. Kaufman, J. H., Colaneri, N., Scott, J. C. & Street, G. B. (1984) *Phys. Rev. Lett.* **53,** 1005–1008.
27. Yakushi, K., Lauchlan, L. J., Clarke, T. C. & Street, G. B. (1983) *J. Chem. Phys.* **79,** 4774–4778.
28. Morris, A. C., Munn, L. T. & Anderson, G. (1942) *Can. J. Res. Sect. B* **20,** 207–211.