Dual-Chemiresistor GC Detector Employing Monolayer-Protected Metal Nanocluster Interfaces

Qing-Yun Cai and Edward T. Zellers*

Engineering Research Center for Wireless Integrated MicroSystems, Departments of Environmental Health Sciences and Chemistry, University of Michigan, 109 South Observatory Street, Ann Arbor, Michigan 48109-2029

The synthesis and testing of two gold−thiolate monolayer-protected (nano)clusters as interfacial layers on a dual-chemiresistor vapor sensor array are described. Responses (changes in dc resistance) to each of 11 organic solvent vapors are rapid, reversible, and linear with concentration at low vapor concentrations, becoming sublinear at higher concentrations. Limits of detection (LODs) range from 0.1 to 24 parts per million and vary inversely with solvent vapor pressure. When configured as a GC detector and used to analyze 0.5-L preconcentrated samples of the 11-vapor mixture, the array provides LODs of ≤700 parts per trillion for most vapors, comparing favorably with those from an integrated array of polymer-coated surface acoustic wave sensors configured and tested similarly. This first report on the use of such an array as a GC detector shows that the combination of response patterns and GC retention times improves capabilities for vapor recognition compared to the sensor array alone or to single-detector GC systems. Spray-coated nanocluster thin films can be deposited reproducibly and exhibit response stability in air that ranges from fair to excellent for up to several months. Scaling the active device area down by a factor of 16 has no significant effect on sensitivity. Implications of these results for portable vapor sensing systems are discussed.

Gas and vapor sensors can be created by depositing interfacial thin films of electronically conducting or semiconducting materials onto patterned microelectrodes and monitoring the change in ac or dc resistance as a function of analyte concentration. Such devices are referred to as chemiresistors, and interfaces consisting of organometallic compounds,[1−3] electrically conductive polymers,[4−6] and carbon-loaded insulating polymers[7−9] have been used to measure various gas-phase species. Arrays of chemiresistors having different partially selective interfaces have been used for vapor or "odor" recognition.[8−11]

Monolayer-protected clusters (MPC) comprise a relatively new class of materials of potential interest in catalysis, molecular electronics, and chemical sensing.[12−18] Typical structures consist of Au cores just a few nanometers in diameter with peripherally bound self-assembling organothiolate monolayers that are soluble in organic solvents by virtue of the organic thiolate capsule, which facilitates processing and thin-film deposition.

These materials exhibit unique electronic and electrochemical properties in solution and in the solid state and have been the topic of considerable research in the past few years (see, for example, ref 16 and references therein). Electronic conduction in thin solid films of these materials occurs by electron tunneling or hopping[13,17,18] and can be altered upon vapor sorption due to swelling or changes in the dielectric properties of the insulating thiolate surface layers.[19] Preliminary studies of Au−thiolate nanoclusters as chemically sensitive layers on chemiresistor vapor sensors reported by Wohltjen and Snow,[19] Evans et al.,[20] and Han et al.[21] have shown that sensitive vapor detection is possible and that the sensitivity depends on the thiol structure and the size of the Au core.

The work described here extends these previous studies by focusing on several practical issues related the use of an MPC-coated chemiresistor array as a GC detector for vapor recognition

---

* Corresponding author: (e-mail) ezellers@umich.edu.

(1) Bott, B.; Jones, T. A. *Sens. Actuators* **1984,** *5* (1), 43−53.

(2) Wohltjen, H.; Barger, W. R.; Snow, A. W.; Jarvis, N. L. *IEEE Trans. Electron. Devices* **1985,** *ED 32* (7), 1170.

(3) Grate, J. W.; Klusty, M.; Barger, W. R.; Snow, A. W. *Anal. Chem.* **1990,** *62,* 1927−1934.

(4) Bartlett, P. N.; Ling-Chung, S. K. *Sens. Actuators* **1989,** *20,* 287.

(5) Slater, J. M.; Paynter, J.; Watt, E. J. *Analyst* **1993,** *118,* 379.

(6) DeWit, M.; Vanneste, E.; Blockhuys, F.; Geise, H. J.; Mertens, R.; Nagels, P. *Synth. Met.* **1997,** *85,* 1303.

(7) Godovski, D. Y.; Koltypin, E. A.; Volkov, A. V.; Moskvina, M. A. *Analyst* **1993,** *118,* 997−999.

(8) (a) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubb, R. H.; Lewis, N. S. *Chem. Mater.* **1996,** *8,* 2298. (b) Severin, E. J.; Lewis, N. S. *Anal. Chem.* **2000,** *72,* 2008−2015.

(9) Patel, S. V.; Jenkins, M. W.; Hughes, R. C.; Yelton, W. G.; Ricco, A. J. *Anal. Chem.* **2000,** *72,* 1532.

(10) Gardener, J. W.; Bartlett, P. N. *Electronic Noses: Principles and Applications*; Oxford University Press: Oxford, U.K., 1999.

(11) Persaud, K. C.; Travers, P. J. In *Handbook of Biosensors and Electronic Noses*; Kress-Rogers, E., Ed.; CRC Press: Boca Raton, FL, 1997; pp 563−592.

(12) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. *J. Chem. Soc., Chem. Commun.* **1994,** 801−802.

(13) Sato, H.; Brown, A. D.; Johnson, B. F. G. *J. Appl. Phys.* **1997,** *82,* 696−701.

(14) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999,** *99,* 1849−1862.

(15) Whetten, R. L.; Shafagullin, N. M.; Khoury, J. T.; Schaaf, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1999,** *32,* 397−406.

(16) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000,** *33,* 27−36.

(17) Snow, A. W.; Wohltjen, H. *Chem. Mater.* **1998,** *10,* 947−949; Chidsey, C. E.; Feldman, B. J.; Lundgren, C.; Murray, R. W. *Anal. Chem.* **1986,** *58,* 601−607.

(18) Wuelfing, P. W.; Green, S. J.; Pietron, J. J.; Cliffel, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **2000,** *122,* 11465−11472.

(19) Wohltjen, H.; Snow, A. W. *Anal. Chem.* **1998,** *70,* 2856−2859.

(20) Evans, S.; Johnson, S. R.; Cheng, Y. L.; Shen, T. J. *Mater. Chem.* **2000,** *10,* 183−188.

(21) Han, L.; Daniel, D. R.; Maye, M. M.; Zhong, C.-J. *Anal. Chem.* **2001,** *73,* 4441−4449.

Table 1. Dimensions of Interdigital Electrode Arrays Used as Chemiresistors[a]

dimension	device type			
	A	B	C	D
electrode spacing (μm)	15	30	15	7
electrode width (μm)	15	20	10	5
electrode thickness (μm)	0.12	0.4	0.4	0.4
overlap length (mm)	4.8	6.0	3.0	1.6
active area (mm^2)	14	30	7.5	1.9

[a] Each device has 50 pairs of electrodes.

and quantification. MPCs of Au−octanethiol and Au−2-phenylethanethiol were synthesized and tested as coatings in a dual-chemiresistor vapor sensor array. The array was then configured as a GC detector in a system consisting of a miniature, thermally desorbed adsorbent preconcentrator[22] and a conventional GC for analysis of vapor mixtures. Response profiles, sensitivities, detection limits, and response patterns are examined for 11 vapors, and comparisons are made with responses from other sensors, particularly polymer-coated surface acoustic wave (SAW) sensors. The reproducibility and stability of sensor responses are also characterized, and a preliminary investigation of device scaling factors as they affect chemiresistor sensitivity is described. The combination of highly sensitive detection of a broad range of volatile organic compounds, pattern recognition of array responses, and chromatographic retention times provides a very powerful approach to the determination of complex vapor mixtures, with important implications for the development of miniaturized environmental monitoring instrumentation.

EXPERIMENTAL SECTION

Chemiresistors were constructed from microelectrode arrays of four different designs, as shown in Table 1. All devices were fabricated on ST-quartz and had 50 pairs of Au electrodes (Cr adhesion layer). Type A devices were obtained from Microsensor Systems, Inc. (Bowling Green, KY). The remaining devices (types B−D) were fabricated in-house by a liftoff process using lithographic masks originally designed to pattern the interdigital transducer electrodes for SAW sensors with nominal operating frequencies of 30, 60, and 131 MHz. The active areas of devices B−D are 30, 7.5, and 1.9 mm^2, respectively (ratio ∼16:4:1), and all have the same electrode thickness of 0.40 μm. Leads were soldered to bonding pads of each sensor, and for all tests, the dc resistance was measured (to ±0.1 Ω) at a rate of 1−2 Hz with a digital multimeter (34401A, Hewlett-Packard, Loveland, CO) at constant current and logged on a benchtop computer using Benchlink Meter software (Version 1.22, Hewlett-Packard).

All reagents and solvents were obtained from Aldrich (Milwaukee, WI) except for sodium borohydride (Acros/Fisher Scientific, Pittsburgh, PA). The Au−n-octanethiol (C8Au) and Au−2-phenylethanethiol (BC2Au) were synthesized by a well-known method,[12,19] using a Au/thiol molar ratio of 4:1 in both cases. Crude products were recrystallized from toluene by addition of ethanol and isolated in >80% yield. Thermal gravimetric analysis showed decomposition onset temperatures of 223 (C8Au) and 225 °C

(BC2Au), similar to those reported for analogous nanoclusters,[17,23] and organic mass fractions of 15% and 13%, respectively, in close agreement with expected mass fractions for a 4:1 Au/thiol stoichiometry.

FT-IR spectra (KBr pellet) are consistent with expected structures[24−26] and confirmed the absence of any phase-transfer agent in the products. A broad background absorbance band from 1000 to 4000 cm^{-1} was observed, which is apparently characteristic of MPC thin films containing relatively large Au particles (i.e., >5-nm diameter).[26,27] TEM analysis showed the products to be polydisperse with average (±SD) diameters of 6 (±1.6) nm for the BC2Au and 8 (±1.9) nm for the C8Au and a moderate degree of agglomeration on the TEM grid−no attempt was made to reduce the size dispersion by digestive ripening.[28]

Films of each MPC were deposited by airbrush from 0.2% toluene solutions while the device resistance was monitored. The relationship between dc resistance and coating mass for different devices and materials was estimated by calibration against microbalance (Cahn 29, Cahn Instruments, Inc. Cerritos, CA) measurements of glass cover slips coated in parallel with operating devices. Profilimetry (Dektak II, Veeco, Plainview, NY) provided thickness values of representative films of known resistance and areal density, from which the effective densities of as-deposited films of both C8Au and BC2Au were determined to be ∼1.2 g/cm^3.

For certain vapor exposure tests, the individual chemiresistors were placed in a large (0.25-L) stainless steel chamber, while for others, two chemiresistors (one coated with BC2Au and the other coated with C8Au) were sealed within a glass cell fashioned from microscope slides, sealed with silicone adhesive and having a dead volume of ∼60 μL. The cell was fitted with passivated fused-silica inlet and outlet capillaries (0.25-mm i.d.) as shown for a pair of type C devices in Figure 1.

The sensors were initially exposed to vapors from each of the 11 solvents listed in Table 2 individually generated from a fritted bubbler and diluted to four or five concentrations within the range of 15−2500 ppm in dry air. These solvents were selected because they represent a range of functional-group classes and span a convenient range of vapor pressures. The highest test concentration differed for each vapor, being limited to somewhat lower values for less-volatile compounds, which generally yielded higher responses. Vapor concentrations were monitored in real time with a precalibrated in-line infrared gas analyzer (MIRAN 1A, Foxboro Co., Columbus, OH). A portion of the test atmosphere was periodically directed through the stainless steel chamber or detector cell while the dc resistance of the sensor was monitored. Steady-state responses were collected in duplicate at each con-

(22) Lu, C.-J.; Zellers, E. T. *Anal. Chem.* **2001**, *73*, 3449−3457.

(23) Chen, S.; Murray, R. W. *Langmuir* **1999**, *15*, 682−689.

(24) Hostetler, M. J.; Stokes, J. J.; Murray, R. W. *Langmuir* **1996**, *12* (15), 3604−3612.

(25) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14* (1), 17 -30.

(26) Leibowitz, F. L.; Zheng, W.; Maye, M. M.; Zhong, C.-J. *Anal. Chem.* **1999**, *71*, 5076−5083.

(27) Brouers, F.; Clerc, J. P.; Giraud, G.; Laugier, J. M.; Randriamantany, Z. A. *Phys. Rev. B* **1993**, *47*, 666−673.

(28) (a) Mohamed, M. B.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. A* **1999**, *103*, 10255−10259. b) Lin, X. M.; Sorensen, C. M.; Klabunde, K. J. *J. Nanopart. Res.* **2000**, *2*, 157−164.

Table 2. Chemiresistor Response Parameters Obtained without Preconcentration along with Similar Data for Two Polymer-Coated SAW Sensors

| | | | sensitivity (LOD)[a] | | | |
| | | | CR | | SAW | |
vapor	p_v (Torr)	approx linear range (ppm)	C8Au	BC2Au	PIB	OV-25
1 ethanol (EOH)	58	60−1600	5.6 (3.2)	1.6 (21)	−	−
2 acetone (ACE)	231	60−2000	1.0 (17)	1.4 (24)	−	−
3 2-butanone (MEK)	72	20−800	5.4 (3.1)	6.4 (5.2)	0.28 (161)	0.47 (95)
4 isooctane (IOC)	49	40−800	26 (0.7)	7.0 (4.7)	1.3 (34)	0.39 (114)
5 trichloroethylene (TCE)	47	20−800	24 (0.7)	13 (2.5)	1.4 (32)	1.3 (34)
6 1,4-dioxane (DOX)	40	20−800	22 (0.8)	26 (1.3)	0.94 (48)	1.7 (27)
7 toluene (TOL)	28	20−800	55 (0.3)	28 (1.2)	2.1 (22)	2.0 (23)
8 perchloroethylene (PCE)	18	20−800	56 (0.3)	30 (1.1)	−	−
9 n-butyl acetate (BAC)	12	20−400	57 (0.3)	57 (0.6)	3.0 (15)	4.6 (9.8)
10 chlorobenzene (CLB)	12	20−800	99 (0.2)	38 (0.9)	4.7 (9.5)	5.5 (8.2)
11 m-xylene (XYL)	8	20−400	182 (0.1)	86 (0.4)	7.0 (6.4)	5.5 (8.2)

[a] Chemiresistor (CR) sensitivities were determined from the slopes of the calibration curves (R_{ppm} vs the vapor concentration, in ppm, C_{ppm}) by linear regression with forced zero ($r^2 > 0.98$ in all cases). SAW sensor sensitivities are taken from ref 29 and are reported as Hz/ppm, assuming a polymer layer thickness equivalent to a 200-kHz frequency shift. LODs are in units of ppm. Dash indicates no data available for comparison.
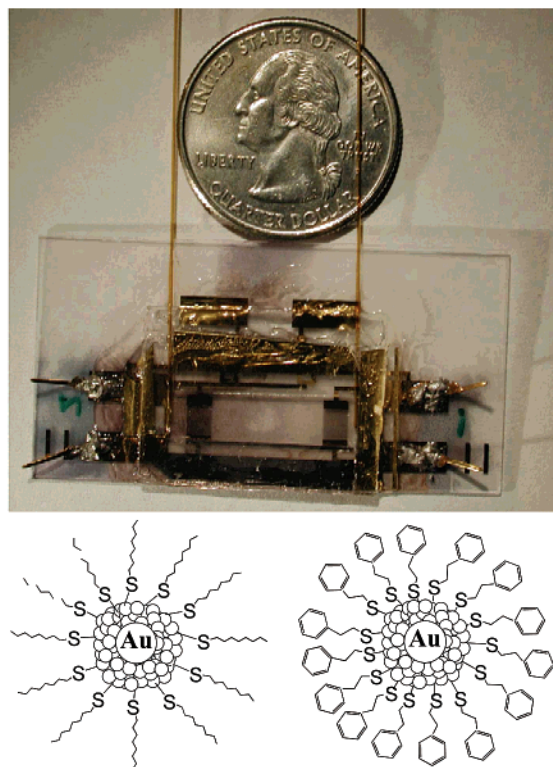

Figure 1. Dual-chemiresistor array housed in a 60-μL detector cell and idealized structures of the C8Au (left) and BC2Au (right) nanoclusters used as interface layers.

centration followed by purging with dry air. For these tests, separate series of exposures were run for each sensor/vapor combination.

The detector cell was then connected to the outlet of a standard bench-scale GC (model HP-6890, Agilent Technologies, Wilmington, DE), and responses were collected from each sensor individually for replicate exposures. For these experiments, test atmospheres containing the 11-vapor mixture, each vapor at 100 or 200 ppm in dry air, were generated in separate Tedlar bags and aliquots of 0.05−10 mL were transferred by gastight syringe into a dry-air stream drawn at 0.05 L/min by a small diaphragm pump

through a dual-adsorbent capillary minipreconcentrator.[22] After collection of 0.5 L, which translates to the mass equivalent of vapor concentrations of 10−4000 ppb, the preconcentrator was rapidly heated to 300 °C and the vapors were backflushed via a six-port valve to the head of the GC column (30-m, 0.32-mm-i.d., 0.25-μm-thick HP-5 stationary phase) under a positive pressure of clean, dry air at 5.6 mL/min. The GC column was maintained at 35 °C for 2 min and then ramped to 70 °C at 15 °C/min. The detector cell temperature was 24 ± 0.5 °C (i.e., room temperature).

RESULTS AND DISCUSSION

Sensor Response Characteristics. Prior to testing the dual-sensor array as a GC detector, an initial series of experiments was performed using two type C devices (Table 1) coated with BC2Au and C8Au, respectively, and housed in the detector cell. The BC2Au coating was applied until the resistance measured 270 kΩ, which corresponds to a deposited mass density of 0.22 μg/mm^2 and a thickness of 0.18 μm. The C8Au coating resistance was 450 kΩ, and the areal density and thickness were 0.26 μg/mm^2 and 0.22 μm, respectively. Exposures were allowed to continue until attainment of sorption equilibrium. Rise and recovery times (90%) were equivalent and were similar for a given vapor on both sensors, ranging from 5 to 11 s among all of the vapors except for isooctane on the BC2Au-coated sensor, which gave an anomalously long response time of 17 s (for reference, the theoretical 99% mixing time for a well-mixed 60-μL volume at a 10 mL/min input flow rate is 1.5 s). Representative response profiles and calibration curves are shown for butyl acetate in Figure 2. For Figure 2b, the change in resistance, ΔR, has been normalized by the initial coating-film resistance value, R_{film}, and multiplied by 10^6. We refer to this throughout the article as R_{ppm}.

Responses varied linearly with vapor concentration at low concentrations but invariably became less sensitive at higher concentrations (see Figure 2). The sensitivities and limits of detection (LODs) in Table 2 were derived from data collected within the linear response range, and the highest test concentrations listed in the table provide a rough estimate of the upper end of the linear range. Vapors giving higher responses tended to have a narrower linear response range. It is noteworthy that
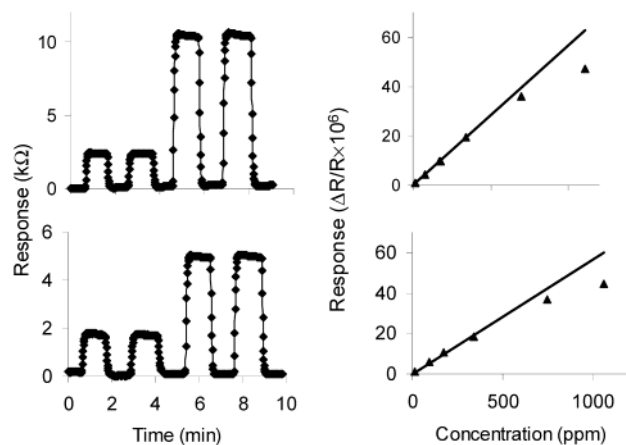
Figure 2. Butyl acetate response profiles (left) and calibration curves (right) for chemiresistors coated with C8Au (top) and BC2Au (bottom).

Figure 3. GC detector traces from (a) FID, (b) BC2Au CR, and (c) C8Au CR for an 11-vapor mixture. Numbers correspond to the vapors listed in Table 3.

the responses to ethanol, as with all vapors, were positive (i.e., increased resistance) in contrast to results reported by Wohltjen and Snow for propanol[19] and by Evans et al. for methanol and ethanol[20] for nanoclusters of similar composition. In the former case, this can be attributed to the use of an ac voltage and consequent influence of capacitive effects. Replicate analyses were highly reproducible, yielding relative standard deviations (RSDs) of < 2%.

LODs, calculated as three times the baseline rms noise level, which was ~3 Ω for both sensors with the coating thicknesses used in these initial tests, ranged from 0.1 (xylene/C8Au) to 24 ppm (acetone/BC2Au) (Table 2) and decreased with decreasing vapor pressure among the solvents tested, reflecting the importance of vapor partitioning into the interfacial film.[29] Sensitivities are comparable to those reported by Wohltjen and Snow and by Han et al. for analogous sensor−nanocluster combinations,[19,21] and appear to be considerably greater than those reported for chemiresistors coated with carbon-loaded insulating polymers.[8,9]

The LODs presented in Table 2 and the sensitivities from which they were derived can be compared to those for two polymer-coated SAW sensors obtained from the literature[29] for vapors common to both studies. The polyisobutylene (PIB) SAW sensor coating should provide vapor sorption interactions similar to those of the C8Au, and the OV-25 (poly(triphenylmethylsiloxane)) SAW sensor coating should provide interactions similar to those of the BC2Au. In all cases, the CR sensors provide higher sensitivities and lower LODs, with the LOD ratios ranging from 10 to 90 in favor of the CR sensors. The ratios of sensitivities for the two SAW sensors (PIB/OV-25, thickness normalized) to those for the two CR sensors C8Au/BC2Au for these vapors were roughly similar.[21]

GC Detector Performance. As a GC detector, the MPC-CR array exhibited good peak shapes and highly reproducible responses (RSD < 1%, $n \geq 3$). Figure 3 compares detector response traces for a standard FID and the two MPC-CR sensors. Sensor response peaks are somewhat broader than those from the FID. Peak broadening can be ascribed to a combination of the larger dead volume in the sensor array cell and connecting tubing, the low temperature of the array, which may increase
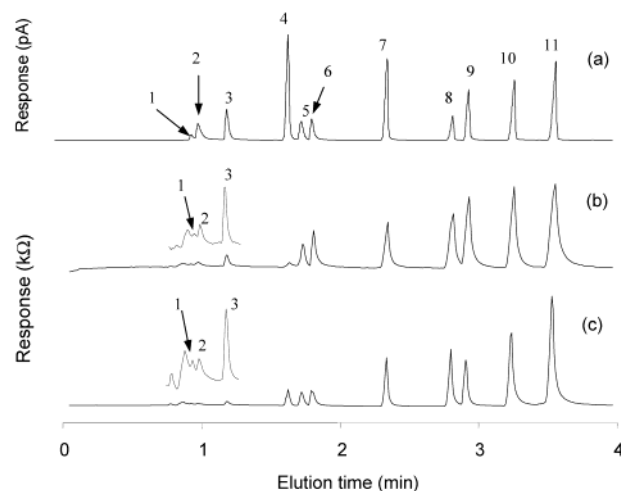
nonspecific adsorption, and the finite vapor sorption/desorption kinetics of the sensor coatings. Similar peak shapes have been observed with an integrated polymer-coated SAW sensor used as a GC detector.[22,30]

For the 0.5-L sample volumes analyzed, peak heights were linear with concentration over the ranges of concentrations shown in Table 3 ($r^2 \geq 0.98$). Above these concentrations, the sensitivity declined (i.e., responses increased at a lower rate) as observed in calibrations without preconcentration/separation. The onset of nonlinearity also occurs earlier with vapors to which the sensors were more sensitive.

Comparing LODs under these conditions to those obtained without preconcentration gives an average sensitivity enhancement (i.e., preconcentration) factor of ~1200 (range 720−1580), which is similar for a given vapor for both sensors, with somewhat higher values being observed for the lower molecular weight compounds. Isooctane showed unusually low enhancement factors that differed between the two sensors: 400 with the BC2Au-coated sensor compared to 950 with the C8Au-coated sensor. Variations in enhancement factors arise from differences in chromatographic peak broadening or sorption kinetics in the sensor interface layers. However, the relative responses for the two CR sensors were about the same regardless of preconcentration, indicating similar effects on both sensors for a given vapor. Of course, further enhancements would be expected with larger preconcentration volumes, but 0.5 L represents a sample volume that could be conveniently collected within a few minutes with miniature sampling pumps.

Table 3 also lists LODS obtained from a parallel study of an integrated array of polymer-coated SAW sensors also used as a GC detector[30] for the six vapors common to both studies. Since the SAW sensor array data were obtained using a preconcentrated sample volume of 1 L, LOD values were doubled prior to entry in Table 3. The SAW sensor array was calibrated at 2 mL/min and has a detector cell volume of only ~2 μL. The dependence of sensitivity on flow rates and dead volumes for both sensor arrays precludes a rigorous comparison. Nonetheless, these represent

(29) Patrash, S. J.; Zellers, E. T. *Anal. Chem.* **1993**, *65*, 2055−2066.

(30) Lu, C.-J.; Zellers, E. T. *Analyst*, in press.

Table 3. Limits of Detection Obtained from Chemiresistor and SAW Sensors Configured as GC Detectors from 0.5-L Preconcentrated Vapor Samples

| | | LOD (ppb) | | | |
| | | CR | | SAW[a] | |
vapor	approx linear range (ppb)	C8Au	BC2Au	PIB	BSP3
1 ethanol (EOH)	10–1000	3.5	21	–	–
2 acetone (ACE)	40–4000	12	16	>100	6.7
3 2-butanone (MEK)	10–2000	2.2	3.4	–	–
4 isooctane (IOC)	10–1000	0.7	12	–	–
5 trichloroethylene (TCE)	40–2000	0.6	2.1	40	2.7
6 1,4-dioxane (DOX)	10–1000	0.7	1.3	–	–
7 toluene (TOL)	10–1000	0.3	1.1	46	2.8
8 perchloroethylene (PCE)	10–1000	0.3	1.0	–	–
9 n-butyl acetate (BAC)	10–500	0.2	0.6	33	0.5
10 chlorobenzene (CLB)	10–1000	0.2	0.7	21	1.2
11 m-xylene (XYL)	10–500	0.1	0.5	15	1.0

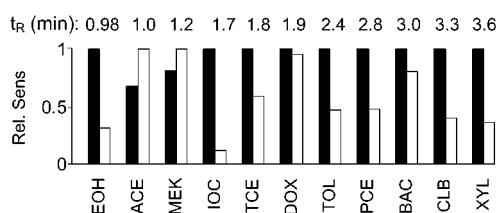[a] Reference 30; dash indicates no data available for comparison.

Figure 4. Normalized response patterns for each vapor from the MPC-CR sensor array (C8Au, filled bar; BC2Au, open bar) along with GC retention times (t_R) for an 11-vapor mixture (see Table 3 for acronym definitions).

more or less typical operating conditions for each sensor type, making the data worth considering together.

LODs for the MPC-CR array are consistently significantly lower than those for the PIB-coated SAW sensor by factors of 70–150 (C8Au) and 20–50 (BC2Au) and are comparable to or lower than those for the BSP3-coated SAW sensor. The latter SAW sensor coating provides unusually high sensitivity to all vapors, and to hydrogen bond basic vapors in particular, among the polymer coatings tested on this integrated array.[12,30] Thus, the performance of these MPC-CR sensors rivals or exceeds that of the best SAW sensor. Further (fractional) improvements in sensitivity are expected by increasing the MPC layer thickness (see below) and reducing the CR array detector dead volume.

Figure 4 presents the relative response patterns from the MPC-CR array sensors for each of the 11 vapors along with their GC retention times. The pattern for each vapor has been normalized to the largest-responding sensor. The patterns among the aromatic vapors are similar, as are those of the two chlorinated hydrocarbons and the two ketones. However, those vapors having similar response patterns are separated chromatographically, permitting facile recognition and discrimination of mixture components. It is likely that binary coelutions could be tolerated, provided that the response patterns of the coeluents were sufficiently different, since it has been shown that discrimination of dissimilar binary-mixture components (e.g., acetone and ethanol) with a sorption-based two-sensor array can be readily achieved.[31] A preliminary test with a binary mixture of perchoroethylene and n-butyl acetate showed that their composite response is equivalent to the sum of the component vapor responses, which greatly facilitates the analysis of coeluting vapors.

Reproducibility and Aging. Coating reproducibility was assessed in several experiments where the interface layers were applied while monitoring the resistance. Four type C devices were spray-coated with BC2Au to resistances of 56, 57, 64, and 67 kΩ; the first two devices were coated separately and the latter two were coated simultaneously. Subsequent exposure to toluene vapor at several concentrations gave sensitivities (R_{ppm}/C_{ppm}) of 41, 39, 39, and 38, respectively. Tests with the C8Au nanocluster gave similar results, with an RSD of 2% for sensitivity to toluene among three coatings. This shows that fairly precise control of deposition is possible using the airbrush technique and that the resulting interfacial films show highly reproducible sensitivities.

The stability of the coatings was assessed by monitoring R_{film} as well as the sensitivity to toluene vapor over time. The MPC-CR array detector used in the GC experiments described above (Figure 3) were set aside for six months and then retested under the same conditions. The R_{film} values had declined by 5% and 15% for the C8Au-coated device and the BC2Au-coated device, respectively. The corresponding C8Au R_{ppm}/C_{ppm} value for toluene had declined by only 1% while that for the BC2Au had declined by 17%. Similar results were observed for other vapors, implying that changes in response patterns are similar among all vapors. Another series of tests performed over a two-month period confirmed that the base resistance and sensitivity of the C8Au-coated sensor remains stable, while the BC2Au-coated sensor suffers a loss of sensitivity, in this case a decline of 23%. For these latter tests, devices were free-standing and openly exposed to laboratory air during storage and handling, whereas the sensors used as the GC detector were kept within the detector cell. This suggests that the BC2Au is slowly decomposed in air. Although no spectral analyses of the films were performed, there are literature reports of alkanethiolate SAMs on Au surfaces reacting with atmospheric ozone as a mechanism of decomposition, with shorter-chain compounds showing greater instability.[32]

(31) (a) Park, J.; Groves, W. A.; Zellers, E. T. *Anal. Chem.* **1999**, *71*, 3877–3886. (b) Zellers, E. T.; Batterman, S. A.; Han, M.; Patrash, S. J. *Anal. Chem.* **1995**, *67*, 1092–1106. (c) Park, J.; Zhang, G. Z.; Zellers, E. T. *Am. Ind. Hyg. Assoc. J.* **2000**, *61*, 192–204.
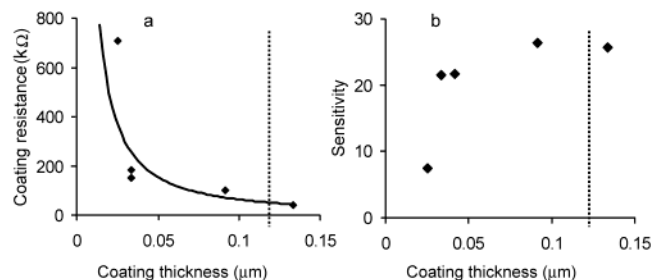(32) Schoenfisch, M. H.; Pemberton, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 4502–4513.

Figure 5. Measured (a) film resistance (R_{film}) and (b) toluene sensitivity (R_{ppm}/C_{ppm}) as a function of BC2Au layer thickness for a series of type A chemiresistors. Vertical dashed line indicates the electrode thickness. Curve in (a) is the best-fit line. No smooth curve could be fit to the data points in (b).

Film Thickness and Device Scaling. Experiments were also performed to probe the effect of design variables on performance. The first issue explored was the MPC nanocluster layer thickness. The following equation describes the dependence of the film resistance on the film thickness:[17a,b]

$$R_{film} = \rho(S/(2n - 1)LH_{film}) \qquad (1)$$

where ρ is the film resistivity, S is the electrode spacing, L is the overlap length of adjacent electrodes, n is the number of electrodes in the array, and H_{film} is the film thickness. It is assumed that the thickness of the interface layer is no more than a few times that of the electrode on the device substrate. Thus, R_{film} should be proportional to $1/H_{film}$. Subsequent vapor exposure will swell the film and may also change its dielectric properties, leading to changes in H_{film} and ρ, but an analytical expression for the expected vapor response has not been derived.

Figure 5a shows the dependence of R_{film} on H_{film} for the BC2Au nanocluster as determined with a series of type A devices. The best-fit curve in Figure 5a gives an correlation coefficient (r^2) of only 0.82. The corresponding plot of R_{film} versus $1/H_{film}$ is linear ($r^2 = 0.92$) if the point corresponding to the thinnest coating is omitted. This point gave a much higher resistance than expected, most likely due to film discontinuities. From the linear portion of the plot, a ρ value of 17 kΩ·cm was calculated via eq 1. A higher, though reproducible, BC2Au film resistivity value was obtained from a series of measurements with the type B–D devices, and the C8Au nanocluster film resistivity was ~8-fold greater than that for the BC2Au film, as expected from the longer alkyl chains in the former material.[18] These ρ values are consistent with those reported previously for alkyl and aryl thiolate nanoclusters.[17,20,26]

Figure 5b shows the corresponding sensitivity to toluene vapor for each of the BC2Au-coated chemiresistors in Figure 5a. The sensitivity increases with increasing film thickness but plateaus at a film thickness comparable to the thickness of the electrode. A smooth curve could not be drawn through these data points. We also observed that the baseline noise level decreases by ~10-fold with increasing film thickness over this range, further favoring the thicker films. However, the response time also increases with film thickness, increasing steadily from 3 to 9 s over the range represented in Figure 5b. Thus, increasing the film thickness beyond that of the electrodes provides no apparent advantage. For the data presented in Tables 2 and 3, the film thicknesses

Table 4. Similarity in Responses for Scaled Devices Coated with BC2Au MPC

parameter	device type		
	B	C	D
relative device area	16	4	1
coating resistance (kΩ)	125	134	135
coating thickness (μm)	0.3	0.3	0.3
$S/[(2n-1)(LH_{film})]$ (mm^{-1})	16.7	16.7	14.7
sensitivity[a](R_{ppm}/C_{ppm})	53	43	41

[a] From calibration with toluene vapor ($r^2 > 0.99$).

were about half of the electrode thickness, suggesting that fractionally higher sensitivities might be realized.

In a separate experiment, three devices, one each of type B–D, were coated simultaneously with BC2Au until the resistance change reached the values shown in Table 4 (only device B was monitored in real time). The film thickness was calculated to be ~0.3 μm, or 75% of the electrode thickness of 0.4 μm. These sensors were subsequently exposed to toluene, giving the sensitivity values shown, which differ by ~20%. Accounting for the apparent differences in coating thickness (mass) as reflected in the R_{film} values, the sensitivities are equivalent within the resolution of the determination. Thus, scaling the device size down by as much as a factor of 16 has no significant effect on sensitivity.

Practical Implications. When operated as a GC detector with vapor preconcentration, the high sensitivities achieved with the MPC-coated chemiresistor sensor array, relative to other competing sensor array technologies, favor its use in miniaturized portable vapor analysis systems for monitoring indoor or ambient environmental air quality, for example, where detection of low- or sub-part-per-billion concentrations of complex mixtures are desired. The relatively small sample volumes required translate into reduced pumping rates or analytical duty cycles. Further improvements in sensitivity are expected by optimizing coating thicknesses and reducing the detector dead volume.

The finding that response patterns from this simple array are qualitatively similar to those from polymer-coated SAW sensors and that the composite pattern from a binary vapor mixture was equivalent to the sum of the component vapor patterns suggests that certain coelutions may be tolerated from the separation stage while still maintaining the ability to identify (recognize) the coeluting species.[31] For field instrumentation, this would permit more rapid separations and less concern about peak broadening.

Although the sensor coated with the shorter-chain, aromatic-thiol nanocluster showed a reproducible decline in sensitivity that may be indicative of oxidative decomposition, the sensitivity changes observed were gradual and were similar among several vapors. This suggests that they could be compensated for via periodic calibration. We are currently exploring other MPC structures as well as developing an integrated array for reducing detector dead volume.