CHEMIRESISTOR ARRAY WITH NANOCLUSTER INTERFACES AS A MICRO-GC DETECTOR

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ABSTRACT

An integrated array of chemiresistor (CR) microsensors employing a novel set of Au-thiolate monolayer-protected nanoclusters (MPN) as interface materials has been developed and tested as an ultra-low-dead-volume detector for a micro gas chromatograph (μGC). Six MPNs 3-5 nm in mean core diameter each with a different type of organo-thiolate ligand were synthesized by a single-phase method, spray cast onto interdigital electrodes, and exposed to several organic vapors. Four of these MPNs were coated onto the same CR array and used as a detector for a conventional GC to analyze a mixture of 15 vapors. The array provides characteristic vapor response patterns, linear calibration curves, and good overall sensitivity, which increases at lower temperatures and detector-cell flow rates. On the basis of injected mass, GC responses indicate that detection limits in the low part-per-trillion range are achievable from preconcentrated sample volumes of < 1 L. Sensitivity does not vary significantly among similarly coated CRs having electrode spacings ranging from 0.1 – 15 μm consistent with a response model based on bulk-film swelling.

INTRODUCTION

Most microsensor arrays designed for the determination of volatile organic compounds (VOCs) rely on reversible, partially selective partitioning of the vapors into sorptive (e.g., polymeric) interfacial films on the sensors in the array [1]. Detection limits are generally in the mid-to-low part-per-million range for organic compounds with vapor pressures above 1 torr, regardless of the sensor type or transduction mechanism. Although discrimination among individual vapors can be achieved by use of different interfacial materials or transducers in the array followed by pattern recognition analysis [2,3], only a few vapors can be determined simultaneously because of the limited selectivity inherent in the reversible non-bonding vapor-interface interactions governing the responses [4]. These limitations impose the need for preconcentration and gas chromatographic (GC) separation in order to perform complex-mixture analyses of low-level environmental VOC contamination [5,6]. Recent advances in microfabrication have facilitated production of tightly-packed multi-sensor arrays that can be housed in low-dead-volume detector cells [3,5,7], which is important in GC to minimize band broadening and required sample mass. MEMS preconcentrators and separation columns have also been described [7-9].

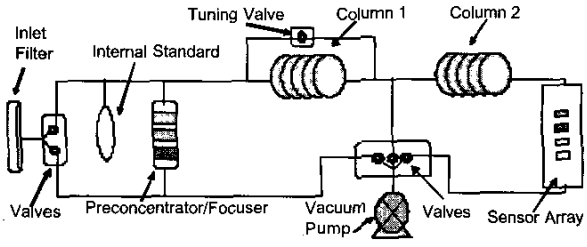

Figure 1. Schematic diagram of a μGC.

This paper describes part of an effort to produce a low-power MEMS micro gas chromatograph (μGC) for environmental and homeland security applications that will ultimately occupy a volume of ~1cm^3 and be equipped with two-way wireless communication for extended, remote operation. A block diagram of the μGC design is shown in Figure 1. In operation, filtered air samples are drawn through a micro-preconcentrator/focuser (μPCF) [7] where vapors are trapped and subsequently thermally desorbed/backflushed into the two-stage, tunable separation module [5,9]. Resolved, or partially resolved vapors then elute through the detector cell containing an integrated array of chemiresistor (CR) sensors whose collective response spectrum can be combined with retention time information in an artificial neural network system to identify the eluting vapors.

The chemiresistor array employs interfacial films of Au-thiolate monolayer-protected nanoclusters (MPN) whose dc resistance increases upon swelling by sorbed vapors. Several researchers have explored their vapor sensing properties and performance [10-14]. A recent study from this laboratory on a GC detector comprising two discrete CRs established the feasibility of such a GC detection scheme and also looked at scaling factors and film-thickness effects [14].

In a continuation of that work, this paper reports on the performance of an integrated array of CR sensors employing some previously unreported MPNs synthesized by a novel single-phase method. Sensor characterizations are presented as a function of several design and operating parameters related to the use of an array of MPN-coated CR sensors as a μGC detector.

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EXPERIMENTAL

Synthesis and Characterization. The most common method for Au-thiolate MPC synthesis is that of Brust et al. [15], which requires an ionic phase transfer catalyst that is difficult to remove from the final product [16]. Residual catalyst is expected to affect electronic conduction in MPN films. For the present study, this problem was avoided by use of a single-phase synthetic method that does not rely on such a catalyst and whose details will be reported elsewhere.

MPNs with various thiolate ligands were synthesized, but many were not tested extensively because of instability, prohibitively high film resistances, insolubility, or other reasons. The original design strategy was to make ligands with functionalities that spanned the vapor-interaction types embodied in the linear solvation energy relationship models [2]. Ligand facilitation of electronic conduction was a secondary consideration.

Of the 6 MPNs studied (Figure 2), all but AuCCN were made by direct addition of the corresponding thiol to a solution of a Au(III) salt in the presence of a reducing agent. AuCCN was produced by a ligand place-exchange reaction [17] of AuC8 with 7-mercaptoheptanitrile. All MPN materials were purified and examined by UV-vis, TEM, FT-IR, TGA, and ^{1}H-NMR.

Detector Fabrication and Testing. Most tests used the integrated 4-CR arrays shown in Figure 3. Each sensor consists of 20 pairs of interdigital Au/Cr electrodes: 1.4 mm (overlap length) x 15 μm (width and space) x 0.4 μm (thickness) deposited on a Si substrate with a thick layer of insulating thermal oxide. Additional tests were performed with devices having electrode spacings of 0.1, 0.3, and 1 μm and different numbers of electrodes. Connecting pins were soldered to the bonding pads and inserted into sockets mounted on a PC board. Sensors were treated with a series of solvents and then an air-plasma prior to film deposition. MPN films were spray deposited from dilute solutions in an organic solvent and annealed at 70 °C and 10 kPa for 2 hr. Film resistance was monitored during deposition. For initial tests of steady-state responses, all four sensors in an array were coated with the same MPN and exposed in a 0.24-L stainless-steel chamber to repeated cycles of vapors at concentrations ranging from 10-1500 ppm in dry air. Subsequent tests were conducted with a different coating on each sensor, both in the chamber and then with the array enclosed by a Macor lid fitted with fused-silica inlet/outlet capillaries and bonded to the substrate with UHB tape (3M Corp.) to create a detector cell with a dead volume of ~3 μL. A thermoelectric cooler was used for reducing the sensor temperature for certain tests. Sensor responses were quantified and compared by dividing the observed change in dc resistance by the pre-exposure baseline resistance and multiplying by 10^6 (R_{ppm}). This normalizes for electrode geometry so that sensitivities are indicative of the change in film resistivity.

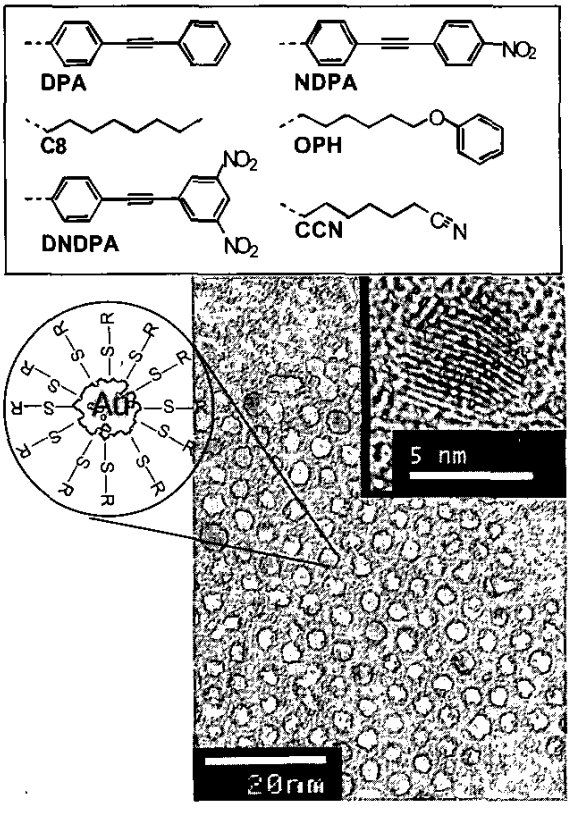

Figure 2. TEM image of Au-C8 MPNs and idealized MPN structure (lower panel); structures of organic portion ("R-groups") of the 6 MPNs examined.

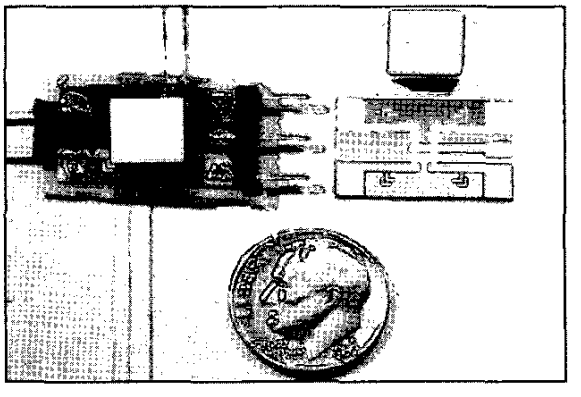

Figure 3. μGC detector assembly comprising an integrated 4-chemiresistor array with nanocluster interface layers, low-dead-volume cell, and capillary inlet/outlet

Resistance measurements were recorded with a multiplexed precision digital multimeter (Agilent 34970a). For GC detector experiments where the data acquisition rate is more critical each sensor was made part of a voltage divider circuit with a series reference resistor of comparable value to that of the coated sensor driven at a constant potential of 6V. Since the resistances of the

sensors were high, the bridge output voltages were passed through the non-inverting inputs of zero-gain high-input impedance operational amplifiers to convert the signal to a low-impedance voltage prior to the 16-bit data acquisition board. Data were processed in Grams/32 (AI 6.00, Galactic Industries). Baseline corrections were made as necessary and noise was treated by a 20 point binomial smoothing.

RESULTS AND DISCUSSION

Material Properties. Au core diameters, measured by TEM, ranged from 3.0+/-0.9 nm (AuDNDPA) to 4.3±0.9 nm for (AuC8, Figure 2, lower panel). The organic monolayers give rise to the following characteristic IR absorbances for the MPNs (KBR pellet): 2917 and 2846 cm^{-1} for AuC8; 3027, 2917, 2850, and 1244 cm^{-1} for AuOPH; 3044, 3017, 2204, and 1490 cm^{-1} for AuDPA; 2209, 1593, 1513,1490, 1340 cm^{-1} for AuNDPA ; 3087, 2205, 1540, 1448, and 1344 cm^{-1} for AuDNDPA; and 2921, 2852, and 2242 cm^{-1} for AuCCN. TGA indicated organic fractional masses ranging from 63-85% and decomposition onset (initial mass loss) temperatures > 200 °C in all cases, consistent with reports on other MPNs [14]. MPN solubilities vary with the ligand structure, but are generally soluble in moderately polar organic solvents.

Sensor Response Characteristics. Precise relationships between the mass, thickness, and resistance of coated MPN films were not available at the time of this report. Coating was continued until the observed resistance ceased to change (decrease) upon further passes with the airbrush. Baseline resistances after annealing ranged from 25 kO to 30 MO and although generally reproducible to within 15% among four simultaneously coated sensors, exceptions were observed. Assuming that film thicknesses are equivalent to the electrode thickness, film resistivities [14] range from 6 kO-cm to 3.4 MO-cm among these MPNs. Interestingly, resistivities of the three MPN materials with DPA-derivative ligands were comparable to or greater than those of MPNs with substituted alkyl ligands.

Calibrations were performed with the following individual vapors: methyl ethyl ketone (MEK), isopropanol (IPA), toluene (TOL), butyl acetate (BAC), and n-octane (NOC). Response and recovery times (90%) were = 4 s, which is on the order of the mixing time of the chamber, except for the AuDNDPA sensors (~ minutes). Calibration curves were linear over the concentration ranges tested and intersected the origin. Limits of detection, with no data smoothing, ranged from 0.5 ppm (BAC/AuDPA) to 150 ppm (IPA/AuC8). Slope sensitivities to toluene (R_{ppm}/C_{ppm}, where C_{ppm} is the vapor concentration) were consistent to within 7% among the 4 replicate coatings of a given MPN with the exception of AuCCN (20%), in spite of differences in baseline film resistance. Results of correlation analysis, coupled with response time and sensitivity considerations led to the selection of AuC8, AuDPA, AuOPH, and AuCCN MPNs for further testing. The relative response patterns of these sensors for the five test vapors are shown in Figure 4. The diversity of responses appears to be comparable to or better than those obtained with polymer-coated acoustic-wave sensors [14].

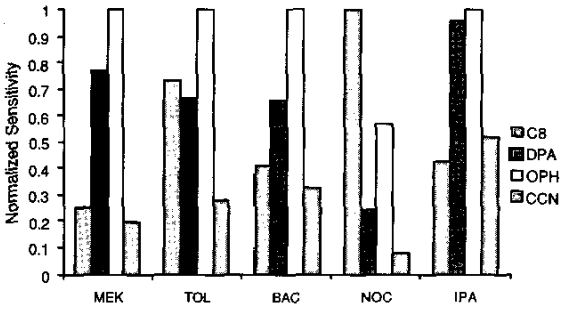

Figure 4 Relative response patterns for five representative vapors from four MPN-coated CR sensors (see text for acronym definitions).

GC Detector Performance. Figure 5 shows the set of 15-vapor chromatograms obtained from the array at 27.5 °C when used as the detector for a conventional GC (Agilent 6890) equipped with a 30-m capillary separation column, and operated with air as carrier gas at 1.3 mL/min. Peak shapes are excellent with no evidence of tailing or excessive broadening relative to flame-ionization detector responses collected in parallel. The vapor concentrations were all ~500 ppm and were injected through a 0.1-mL gas sampling loop. Injected masses therefore are equivalent to those that would be obtained from a 1-L preconcentrated air sample at vapor concentrations of 50 parts-per-billion. Assuming a 1-L preconcentrated air sample had been collected, calculated detection limits derived from the peaks heights range from 20 parts-per-trillion to 9 parts-per-billion (2.2 mL/min), and are somewhat lower than those we reported previously [14].

Flow rate effects examined from 1.3 mL/min to 4.4 mL/min show that responses increase by factors of ~1.3-3 with decreasing flow rate over this range and differ among the 15 vapors, indicating that responses are affected by sorption kinetics in this flow regime. Cooling the array from 27.5 to 3.2 °C led to increases in sensitivity for all vapor-sensor combinations, with enhancement factors typically in the range of 2-4.

Scaling Factors. Scaling behavior was examined by coating devices having electrodes of different dimensions simultaneously with AuC8 and exposing them to toluene. Single devices having interelectrode spacings of 0.1, 0.3, and 1 μm were tested beside a 4-CR integrated array with spacings of 15 μm. Film resistivity values derived assuming the same film thicknesses varied by < 23% and responses to toluene were linear up to 1000 ppm with slopes that varied by < 30% (typically by less than 10%). These results are consistent with those we reported previously and indicate that responses can be modeled assuming bulk-film swelling by sorbed vapors.

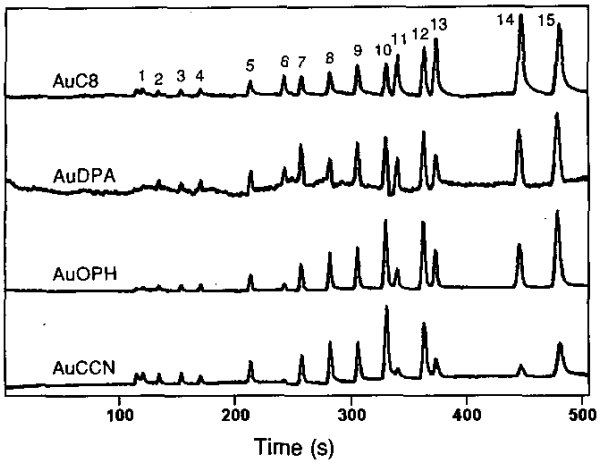

Figure 5 Chromatogram traces from the integrated 4-CR array GC detector (y axis: volts) for a 50 ppb-L injection of the following vapors: 1 IPA, 2 MEK, 3 benzene, 4 TCE, 5 TOL, 6 NOC, 7 BAC, 8 chlorobenzene, 9 m-xylene, 10 2-heptanone, 11 nonane, 12 cumene, 13 a-pinene, 14 decane, 15 d-limonene.

CONCLUSIONS AND FUTURE WORK

We have shown that an integrated chemiresistor array coated with different Au-thiolate monolayer-protected nanoclusters can serve effectively as an ultra-low-volume detector for gas chromatographic analysis. Used in conjunction with an upstream preconcentration device, detection limits < 10 parts-per-trillion appear to be achievable for many VOCs with modest sample volumes. Sensitivity is retained for devices having nano-scale electrode dimensions, which bodes well for further reductions in array size and commensurate reductions in required sample mass. Medium and long-term again studies are underway to explore further the utility of these sensors for distributed environmental sensing. Initial tests performed using MEMS preconcentration and separation components with this array show promising results.

Acknowledgments

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