Monolayer Protected Nanoparticles as Vapor Sensor Array Interface Materials

M. P. Rowe,[a,b] W. H. Steinecker,[a,b] Q. Zhong,[a,c] H. Xu,[a,c] L. A. Farina,[d] C. Kurdak,[d] E. T. Zellers*[a,b,c]

Center for Wireless Integrated Micro Systems (WIMS)[a]
Department of Chemistry,[b] Environmental Health Sciences,[c] and Physics[d]
University of Michigan, Ann Arbor, MI 48109-2029

Several novel modifications, manipulations, and applications of Au-thiolate monolayer-protected nanoparticles (MPNs) related to their ultimate use on integrated vapor sensor arrays in a micro gas chromatographic (µGC) analyzer [1] are described. Vapors partitioning into an MPN film cause it to swell, which increases the electron-tunneling barrier and permits resistance-based vapor sensing [2-6]. We have shown that an array of MPN-coated chemiresistors (CR) can serve as a µGC detector [1,5,6]. However, several aspects of the design and processing of MPNs as sensors materials require optimization. This study explores several of these for the first time including, hybrid-sensor responses; inclusion of Pt-coordination compounds; e-beam patterning; and use of an integrated MPN-coated CR array as the detector in a meso-scale GC for vapor-mixture analysis.

The CR sensor is sensitive to the added volume of sorbed vapors, while a thickness shear mode resonator (TSMR) is sensitive to added vapor mass. The TSMR:CR response ratio, using MPNs with n-octanethiolate ligands (C8-MPN) as interface layers, is highly correlated with the condensed vapor density (Fig. 1). Similar correlations have been observed for carbon-loaded polymer films [7]. This should aid in vapor recognition when using a "hybrid-array" of CR and TSMR (or other mass sensitive) sensors.

Additional transduction mechanisms may be accessible by using mixed interface materials on CR sensors. Combining C8-MPN with the square-planar complex, $PtCl_2$(styrene)(pyridine), results in the expected TSMR mass increase, but a surprising *decrease* in CR film resistance upon styrene vapor exposure. In contrast, ethylbenzene causes the usual increase in resistance (Fig. 2). We ascribe this to the ability of styrene to form a transient complex with Pt through its vinyl group [8], which facilitates charge conduction through the hybrid film to an extent that exceeds the reduction in conduction associated with film swelling. Similar behavior is observed for other olefins and dienes.

Patterning of C8-MPN films by e-beam irradiation has also been explored as part of an effort to create nano-scaled arrays. Sensitivity to toluene vapor declined by ~60% after patterning in early trials, but retained linearity at low concentrations. On-going work is optimizing the e-beam energy to tradeoff nanoparticle insolubility and CR responsiveness for different MPNs.

Practical vapor-mixture analysis has been addressed using a portable meso-scale GC that employs an integrated array of four CR sensors coated with MPNs having the following thiolate ligands: n-octane, diphenylacetylene, phenoxyhexane, and heptanenitrile. Signature vapors collected from the headspace of U. S. paper currency have been preconcentrated, separated, identified from their array response patterns, and quantified in a matter of minutes.

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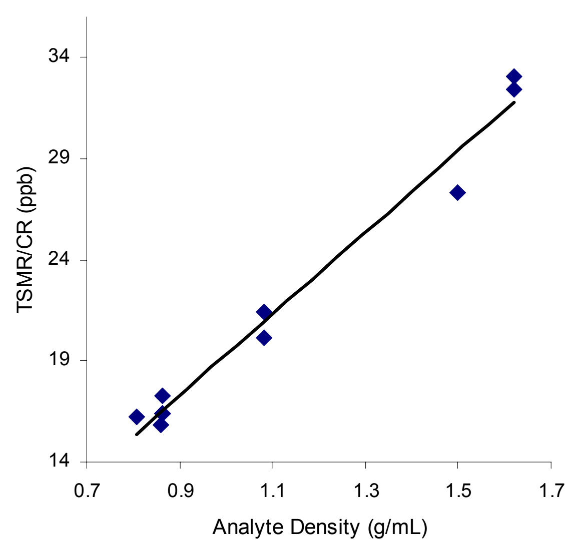

Figure 1. Relationship between TSMR:CR response ratio and analyte density (r^2 = 0.98) with C8-MPN films.

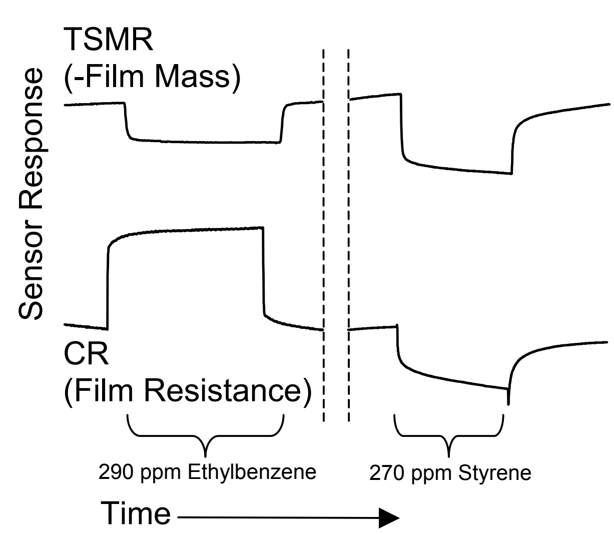

Figure 2.TSMR and CR sensor responses to ethylbenzene and styrene using a C8-MPN + $PtCl_2$(styrene)(pyridine) film. Styrene causes a novel decrease in resistance due to coordination with Pt through its pendant double bond.