

CB NANOSENSORS

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ABSTRACT

A new class of nanometer scale, low power, solid-state devices is being investigated for the detection of hazardous vapors. These chemical vapor sensors are comprised of nanometer-sized gold particles encapsulated by monomolecular layers of alkanethiol surfactant deposited as thin films on interdigitated microelectrodes (Fig. 1). These new, alkythiol-stabilized, gold nanocluster materials are appropriately named metal-insulator-metal-ensembles (MIME).

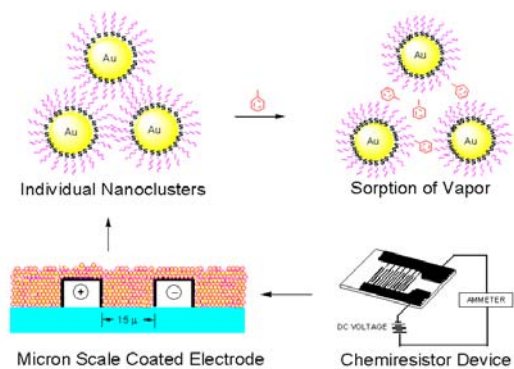


Fig. 1. MIME nanosensor concept.

1. CONCEPT

When chemical (agent, hazmat) vapors reversibly absorb into these thin MIME films, a large modulation of the electrical conductivity of the film is observed (Wohltjen & Snow, 1998). The measured tunneling current between gold clusters is extremely sensitive to very small amounts of monolayer swelling or dielectric alteration caused by absorption of vapor molecules. Response times are controlled by vapor diffusion and are extremely fast for monolayers. Selectivity depends on chemical functionalization of the alkanethiol. For chemical agent simulants, a large dynamic range (5-logs) of sensitivities is observed and extends down to well below sub-ppm vapor concentrations.

2. NANOCLUSTER SIZES

Individual nanoclusters are prepared by the controlled reduction of gold chloride in the presence of suitable alkythiols. As colloidal gold particles form, a monomolecular layer of alkythiol molecules adsorbs on their surface producing a highly stable dispersion of uniformly sized gold particles. Colloidal dimensions (nanometers) are determined by the molecular ratio of gold to alkythiol reactants.

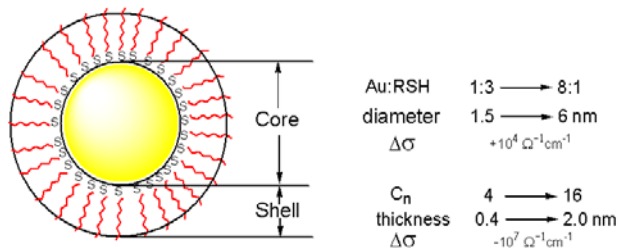


Fig. 2. Sizes & conductivities of gold nanoclusters.

As might be expected for unfunctionalized thiol ligands (Fig. 2), electrical conductivities ($\text{ohm}\cdot\text{cm}^{-1}$) of these nanoclusters increase with an increase in core size or a decrease in ligand shell thickness.

3. SENSOR RESPONSE

An example of the response of a MIME sensor comprised of an 8-carbon alkythiol gold-nanocluster (1:1) to both low and high gas concentrations of toluene is depicted in Fig. 3. In this particular case, the sensor was alternately exposed to calibrated concentrations of toluene and clean dry air, respectively. Rapid, vapor-induced conductivity changes in the MIME device were measured using a square wave excitation. The baseline resistance (zero device signal counts) of this sensor was $1.5\text{M}\Omega$. A small departure from linearity was observed at the higher (>4000 ppmv) concentration ranges.

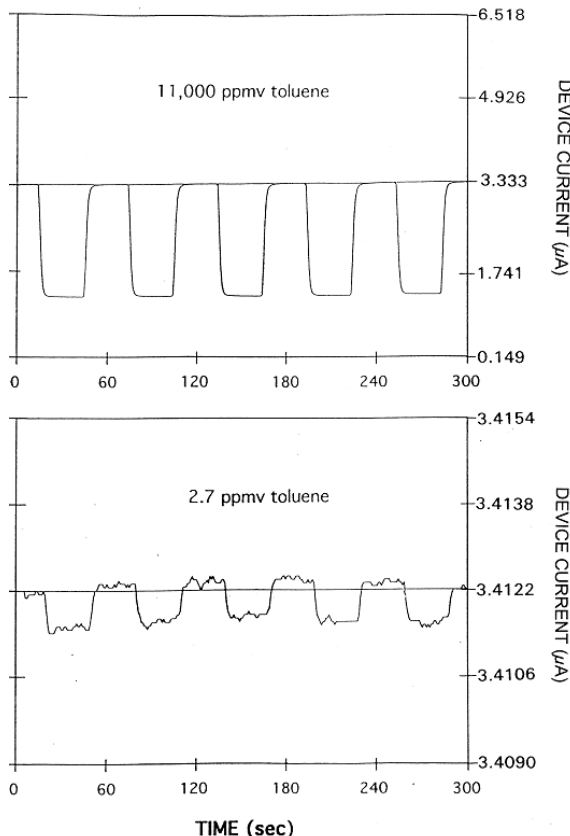


Fig. 3. Response of Au:C₈(1:1) MIME sensor to five 60-s toluene vapor exposure/purge cycles.

4. SELECTIVITY OF NANOCCLUSERS

Tailored selectivities of MIME sensors can be accomplished by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure (Fig. 4).

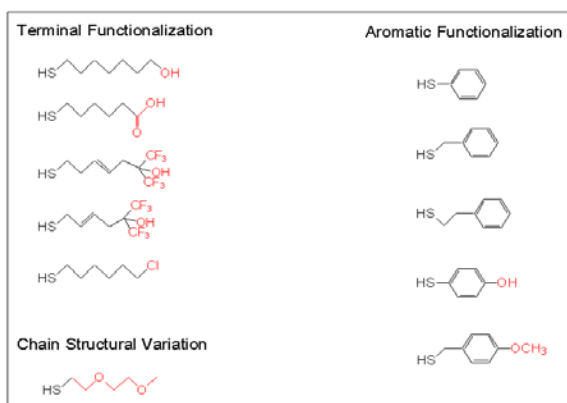


Fig. 4. Functionalized thiol ligands.

As can be seen in Fig. 5, differing responses are observed for the various functionalized MIME coatings. In some cases, in fact, a conductivity *increase* is observed upon exposure. This was observed for

DMMP (dimethyl-methylphosphonate, a nerve-agent simulant) and several nitrogen-containing compounds.

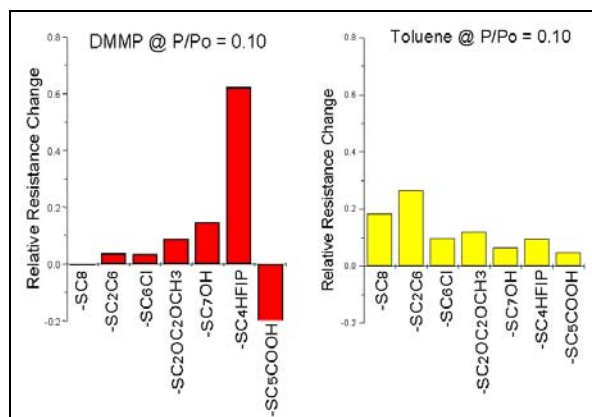


Fig. 5. Relative resistance changes of different MIME coatings exposed to DMMP and toluene.

5. DISCUSSION

A detailed investigation into the mechanism(s) of the electronic charge-transport behavior of the MIME device is currently underway. In a simplistic sense, however, we believe that electron transport most likely occurs via two principal mechanisms: (a) tunneling between the metal clusters (they are spaced <2nm apart with core diameters less than the deBroglie wavelength of electrons in the core) and (b) electron-hopping along the atoms of the thio-alkyl ligand (Snow & Wohltjen, 1998). The insertion of vapor analyte molecules into this “lattice” is likely to have a profound effect on both the tunneling current as well as the electron-hopping current.

Current research efforts are focused on mapping the selectivity and sensitivity of sensor elements. Targeted applications include: low-cost, low-power CB agent sensors, filter residual life indicators and orthogonal detector applications.

ACKNOWLEDGEMENT

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REFERENCES

- Snow, A.W. and Wohltjen, H., “Size-Induced Metal to Semiconductor Transition in a Stabilized Gold Cluster Ensemble”, *Chem. Mat.*, 10, No. 4, 947 (1998).
- Wohltjen, H. and Snow, A.W., “Colloidal Metal-Insulator-Metal Ensemble Chemiresistor Sensor”, *Anal. Chem.*, 70, No. 14, 2856 (1998).