High Performance Metal Oxide Nanostructures for Advanced Solid State Chemical Microsensors

Research underway at NIST, and through collaborations at Northwestern University and South-Ukrainian State University, is aimed at developing nanoparticles, nanofibers, nanowires, nanotubes and related structures of metal oxides for use in microsensor arrays and microanalytical systems to increase sensitivity, selectivity, speed and stability of chemical detection and monitoring. These nanomaterials are being studied as signal transducers for chemical sensors and as elements for upstream filtering and preconcentration of analytes.

K. D. Benkstein, C. S. Mungle, D. C. Meier, S. Garcia and S. Semancik (Div. 836), V. Dravid (Northwestern University), V. Golovanov (South-Ukrainian State University) and A. Kolmakov (Southern Illinois University)

The approach focuses on using individual structures as well as assembled hierarchical structures for chemical sensing applications where high-performance characteristics (e.g., nmol/mol to pmol/mol sensitivity) are required. These well-defined nanostructures will increase the surface area and active interfacial sites for adsorption and reaction of gas-phase analytes, thereby leading to more sensitive chemical measurements. These structures are also manipulated and aligned so as to study scaling (e.g., differences between a single nanowire and several nanowires in parallel) and nanoparticle-to-nanoparticle interaction effects on chemical sensing phenomena.

The driving force behind much of the nano-materials development in the area of chemical sensors is the significant role that the materials surface plays in chemical detection through interaction with analyte molecules. A prime example of the need for highly sensitive and reliable sensors is in homeland security applications, where the detection of trace levels of highly toxic gases is critical.

Specific materials being synthesized and studied include ZnO nanorods, SnO_2, Fe_2O_3 and In_2O_3 sol-gels, and WO_3, Sn and composite Ni-core/TiO_2-shell nanowires. Synthetic methods have been developed based upon the use of chemical additives during nanorod preparation to control the aspect ratios of ZnO nanorods (length:diameter ratios of 5.2 to 0.25, ***Figure 1***). The control is effected by additive interaction with specific crystal faces of the ZnO during nanorod growth, either inhibiting or enhancing growth of particular faces to yield different structures. These ZnO nanorods provide a method to study the effect of particular crystal faces upon analyte interaction with the nanomaterials in sensor operation. Sol-gel materials offer a flexible approach to prepare active sensor materials. In collaboration with the South-Ukrainian State University, sol-gel materials (Fe_2O_3, In_2O_3 and SnO_2) have been evaluated as conductometric sensor films. The initial results suggest that these materials may have some value as highly sensitive active elements in a sensor array.

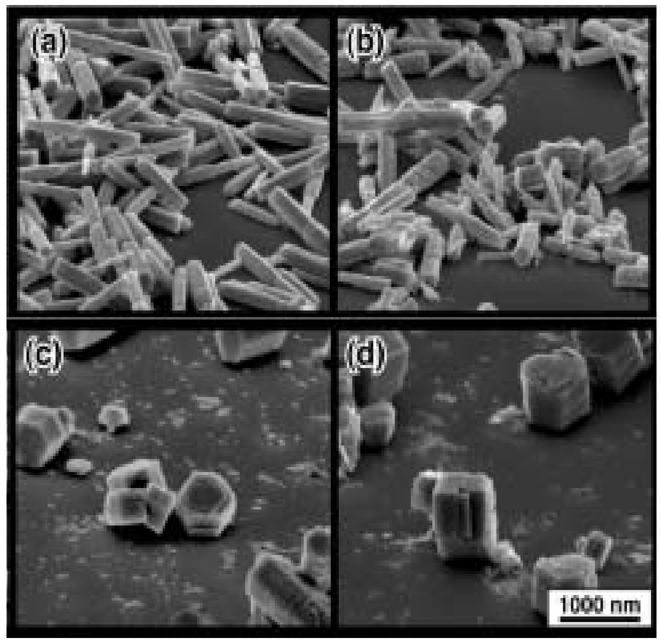

***Figure 1.* SEM micrographs of crystalline ZnO nanorods showing the effects of growth additives on the aspect ratios: (a) no additive, (b) 10 µM, (c) 20 µM, (d) 40 µM citrate additive.**

Additional studies at NIST and at collaborating institutions will elucidate the role of nanostructure and nanomaterials alignment on critical sensor performance parameters, and how further enhancements would be realized through nano-engineering.

Further collaboration with Northwestern University to prepare "nanoline" materials on microhotplate sensor platforms has continued. The nanoline materials offer an alternative method for aligning nanomaterials between electrodes (for other methods being studied, see below), and have the added benefit that they are easily scaled up or down, such that we can study the efficacy of a single nanoline and subsequently add more lines in parallel to study scaling effects. Metal and metal oxide nanowire materials have been synthesized at NIST using porous membranes (50-nm, 100-nm and 200-nm pores) of polycarbonate and TiO_2-coated alumina as templates for electrodepostion. Dielectrophoretic techniques to align the WO_3 and Sn (converted to the oxide after deposition via thermal treatment on the microhotplate) nanowires between electrodes on microhotplate platforms and temperature-controlled gas-phase sensing have been demonstrated ***(Figure 2)***. In addition to dielectrophoretic alignment, magnetic fields have been used to control orientation of nanowire deposition for the Ni-core/TiO_2-shell nanowires. Recent work, in collaboration with Southern Illinois University, has demonstrated the viability of single TiO_2 nanowires as conductometric sensors on microhotplate platforms.

Higher sensitivity, stability, speed and reproducibility of sensing materials are critical to next-generation sensing devices. These improved performance characteristics, attained by proper assembly of nano-building blocks, are expected to impact many application areas including alarm triggers for counter-terrorism, trace gas detection in space exploration and the monitoring of gaseous biologically-generated compounds for medical diagnostics. With the various nanomaterials alignment methods, it will be possible to examine through-wire and across-wire transport, particularly of interest for elucidating the role of grain boundaries (wire-to-wire transport) in chemical sensing. Furthermore, response studies on these aligned nanowires will allow us to perform comparative scaling studies as individual structures are assembled into larger networks and arrays.

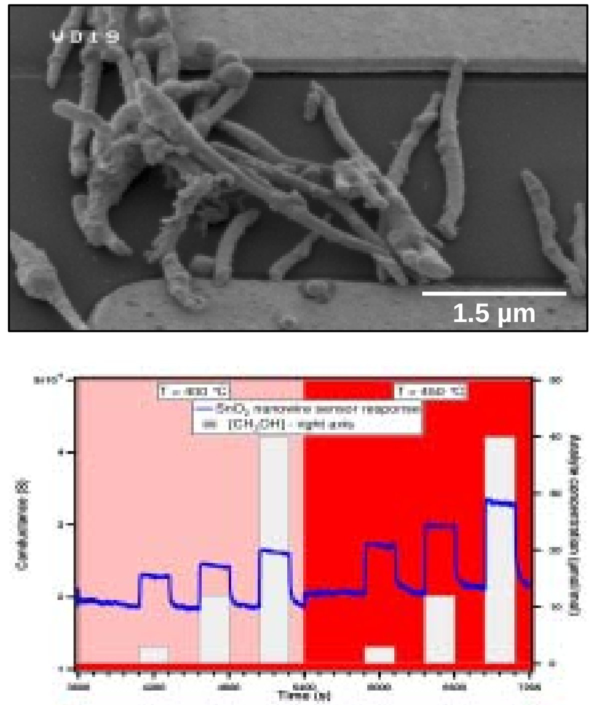

Figure 2. ***SEM micrograph of SnO_2 nanowires dielectrophoretically positioned between electrodes of a microhotplate sensor (top), and the corresponding conductometric sensor response (bottom).***

Publications:

S. P. Garcia and S. Semancik **"Controlling the Morphology of Zinc Oxide Nanorods Crystallized from Aqueous Solutions: The Effect of Crystal Growth Modifiers on Aspect Ratio,"** *Chem. Mater.*, 2006, (submitted).

K. D. Benkstein, C. J. Martinez, G. Li, D. C. Meier, C. B. Montgomery, and S. Semancik **"Integration of Nanostructured Materials with MEMS Microhotplate Platforms to Enhance Chemical Sensor Performance,"** *J. Nanoparticle Res.*, 2006, *8(6)*, 809-822.

K. D. Benkstein and S. Semancik **"Mesoporous Nanoparticle TiO_2 Thin Films for Conductometric Gas Sensing on Microhotplate Platforms,"** *Sens. Actuators B*, 2006, *113*, 445-453.