Nano-Composite Metal Oxides for Electronic Noses

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This program aims at producing the next generation of molecular chemical and biological sensors [1]. Is is an interdisciplinary effort to manufacture electronic "noses" from arrays of nanostructured metal oxide sensors, each of which is specific to a given gas. Specificity in nanostructured oxides is achieved by exploiting their structure sensitivity. The ongoing research focuses on the study of formation mechanisms of the nanostructured sensing probes, on testing their structural and mechanical stability, and on assessing their bio-detection capabilities. New tools for measuring the properties of nanostructured materials are being developed in this program. Collaborations with the Gas Sensor Laboratory at the University of Brescia (Italy) and the Ceramics Laboratory of the Hungarian Academy of Sciences (Hungary) have been developed as part of this work.

Synthesis & characterization of nanostructured probes

***Metal oxide nanowires*:** This project focuses on the synthesis of novel structures of these oxide systems by combining sol-gel processing and electrospinning, thus producing single crystal nanofibers with improved catalytic properties for selective gas detection at lower temperatures. The advantage of producing metal oxide 1D nanostructures lies in the high surface area obtained by such high aspect ratio materials. Any changes in the surface and electronic properties of metal oxides are directly translated to different gas sensitivities. There were two types of metal oxide nanofibers produced by means of electrospinning, those of MoO_3 and WO_3, both of which were incorporated in PVP [2]. It was further possible to obtain pure metal oxide nanowires by decomposing the polymer matrix following a heat-treatment at 500°C for 8 hrs (Figure 1). The resulting oxide nanowires are single crystals, as manifested by the diffraction pattern inserted in figure 1. These are grown along the direction of the decomposed polymer fibers and vary in length from several hundred nanometers to a few μm. Their diameter is close to that of the as-spun fibers. The response of WO_3 equiaxed sol-gel nanograin structures was compared to those of nanofibers produced by electrospinning with regard to their response to low concentrations of NO_2 gas. The nanofibers showed faster response and higher sensitivity; furthermore, the sensors produced offered lower detection limits [2].

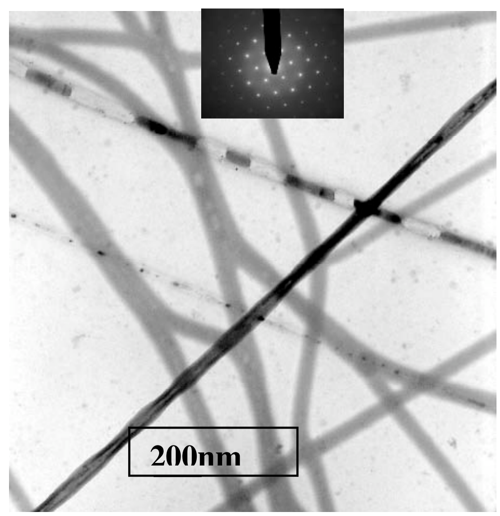

Figure 1: Single-crystal metal oxide nanowires; inset is a selected area diffraction pattern.

Synchrotron XRD experiments: As is well known, synchrotron sources are well collimated and have intensities that are tens of thousands times greater than laboratory sources. The brightness of these sources has opened up new fields of research and allowed for the investigation of very fine structures such as those at the nanoscale. Grazing Incidence XRD (GIXRD) is a particularly suitable technology for thin film characterization [3]. By increasing the path length of the incidence X-ray beam through the film, the intensity from the film can be increased so that conventional phase identification analysis can be carried out. In this project, we have combined the advantages of both synchrotron radiation and the grazing incidence geometry to investigate the structure of the metal oxide nanowires described above [2,4]. We have used the highly collimated synchrotron radiation beam at beamline X18A at the National Synchrotron Light Source at Brookhaven National Lab. The stationary incident beam makes a very small angle with the sample surface (typically 2^{o} to 5^{o}), which increases the path length of the X-rays. A dramatic increase in the film signal-to-noise ratio is achieved [4].

Mechanical property evaluation: The as-spun mats contained a range of volume fractions of oxide nanowires of variable dimensions depending on the processing conditions used. The parameters that were studied involved the precursor solution concentration and the flow rate used during spinning. Increasing the flow rate during spinning increased the average fiber diameter, while increasing the sol-gel volume fraction, increased the viscosity of the mixture, resulting in thinner nanofibers. It is interesting to note that the type of metal oxide sol-gel used also played a role in determining the morphology of the resulting mats. SIEM (Speckle Interferometry with Electron Microscopy) and a tension experiment have been applied to determine the mechanical properties of nanomaterials (e.g. PVP without and with 30% WO_3 at flow rate 10μl/min and 30μl/min). CASI (Computer Aided Speckle Interferometry) algorithm was employed to calculate the displacement field. The Young's moduli of these samples were obtained. It was found that the specimen with the thicker nanowires, also exhibit a higher Young's Modulus and higher strength. The electrospun mats were also found to be highly anisotropic [4].

Nanocomposites as biosensing probes

Enzymes are nature's most specific and selective catalysts. Encapsulation/incorporation of these biomolecules into high surface porous biocompatible polymer mats allows for their higher catalytic activity, faster response and possibly longer lifetime of operation. Urease (E.C.3.5.1.5) was chosen as the model enzyme system in these studies since it acts as a catalyst in the hydrolysis of urea to ammonia and carbon dioxide. Urea is one of the main components of human urine, and waste product that builds up in the blood. Abnormal levels of urea in the blood and urine indicate liver function problems.

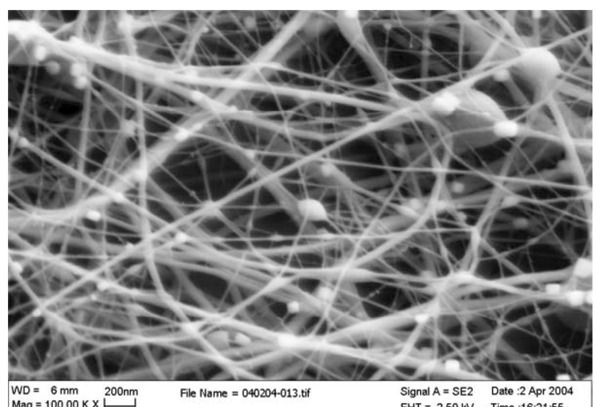

Figure 2: Urease-PVP nanocomposite films for urea sensing.

A novel approach to biosensor development using hybrid nanomaterials systems, such as electrospun polymer/-oxide nanofiber structures in which proteins or cells are incorporated (fig.2), for the selective detection of the bio-species (pathogens) of interest has been demonstrated [5]. The result of the biochemical reactions between the reacting biospecies/bioreceptor is a chemical signal that is sensed by the hybrid nanofiber platform through a conductimetric mode. These new findings open the pathway for numerous applications of the bio-nano-composite materials, including non-invasive medical diagnostics tools, bio-fuel cell devices, protective clothing (electronic and interactive textiles), bioengineering scaffolds and advanced sensor arrays.

Selective Electronic Noses

The use of arrays of chemical detectors has been realized in electronic nose applications [6]. These are electronic devices that typically employ non-selective gas sensitive elements for the monitoring of odors and other gaseous analytes. One drawback in using electronic noses with non-selective gas sensor arrays is that efficient signal processing purposes requires longer response times than what would be needed if selective gas detectors were employed instead. The size of the detector device is larger when sophisticated electronics are required for effective signal processing, thus increasing the load and cost of the device.

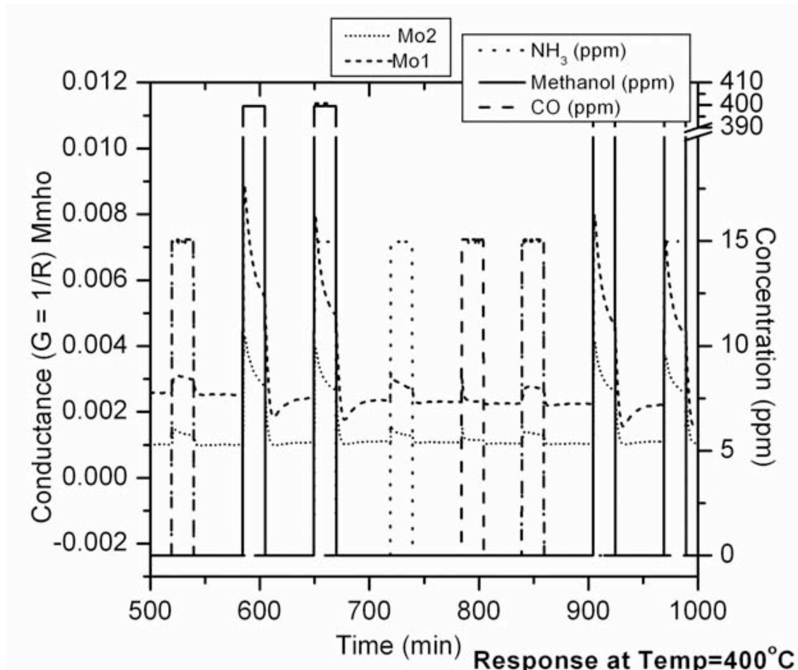

Figure 3: Two-sensor array response to a gas mixture consisting of ammonia, methanol, carbon monoxide and synthetic air as the background at 10% RH.

An alternate approach to chemical detection has been demonstrated through the use of small arrays (2-3 elements) of selective gas sensors (fig. 3). Sensor selectivity is defined here as higher sensitivity to a given gas or class of gases in the presence of interfering gaseous species. Nanocrystalline processing promotes the formation of metastable polymorphs and produces oxide microstructures with high surface area, thus promoting gas adsorption and enhancing gas sensitivity. In order to exploit the polymorphic nature of the oxides used in this study as sensing elements, the sensing films were stabilized and tested at conditions defining the phase stability fields for each of the various polymorphs of these oxides (as determined by means of differential scanning calorimetry techniques) [7].

References

[1] For further information about this project link to **<http://www.matscieng.sunysb.edu/gouma/NIRT/>** or email **<pgouma@notes.cc.sunysb.edu>**
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