Project Overview: Nanoscale Ionization Detectors for Chemical Sensing

NSF NIRT Grant 0403789

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First responders rushing to the site of an emergency require chemical sensors that are compact, light-weight, low-power and can provide sensitive and specific diagnostic signals in real-time mode. Presently there is no portable sensor that meets all of the above requirements.

To overcome this challenge researchers have explored the use of nanotube electrical conductivity based sensors as field-operable (portable) gas analyzers. However there are many practical limitations to the successful implementation of such sensors:

- Nanotube conductivity measurements cannot distinguish one chemical from another.
- It is challenging to identify gases in mixtures; since nanotubes are sensitive to so many different types of chemicals, different gases can be combined in different concentrations to yield the same net change in the nanotube conductance.
- Conductivity measurements cannot be used to identify gas molecules that are unable to exchange charge with nanotubes; for example inert gas species cannot be detected.
- It is not possible to detect species that are incapable of being adsorbed on to nanotubes.
- Chemisorption can cause an irreversible change in the nanotube's conductivity. In such cases, the sensor cannot be used repeatedly and must be discarded after use.
- Nanotube conductance is exquisitely sensitive to environmental conditions (moisture, temperature, flow velocity or contamination) creating difficulties for repeatable sensing.

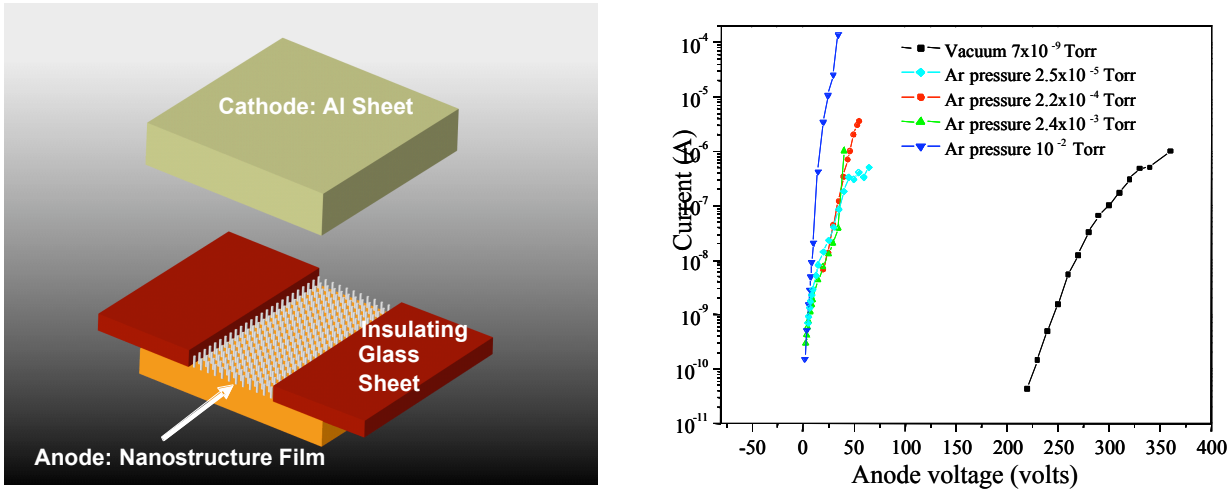

Figure 1: (Left) schematic of the nanoscale gas ionization device. (Right) typical results showing stable ionization discharge for argon at extremely low operating voltages (3-4 Volts).

In this project we are proposing a new approach for sensing which represents a radical departure from traditional nanotube electrical conductivity based measurements. We propose to develop nanoscale field-ionization devices (figure 1 shows a schematic) that use nanostructured electrode arrays to efficiently ionize gas analytes at the fraction of the power of a traditional gas ionizer. The geometry induced electric field amplification effect associated with the sharp tips of the nanostructure allows for ionization at extremely low voltages (see figure 1- right image). The

onset voltage at which ionization takes place is a characteristic of the gas and provides a fingerprint to identify the gas and lower the rate of false alarms which is a major problem with traditional portable gas analyzers. Moreover by reducing electrode spacing to below the gas mean free path, our group has been able to prevent cascade collisions and engineer ballistic transport of ionized gas molecules to the sensing electrode. This can allow for selective ionization of gases in mixtures enabling high sensitivity and high specificity of the recognition. Using this principle we were able to detect a range of gas species (such as He, Ar, N_2, O_2, CO_2, NH_3 etc.) using a compact, low-power and battery operated device. These results [2-3] were published in 2003 in Nature and in 2004 in Applied Physics Letters.

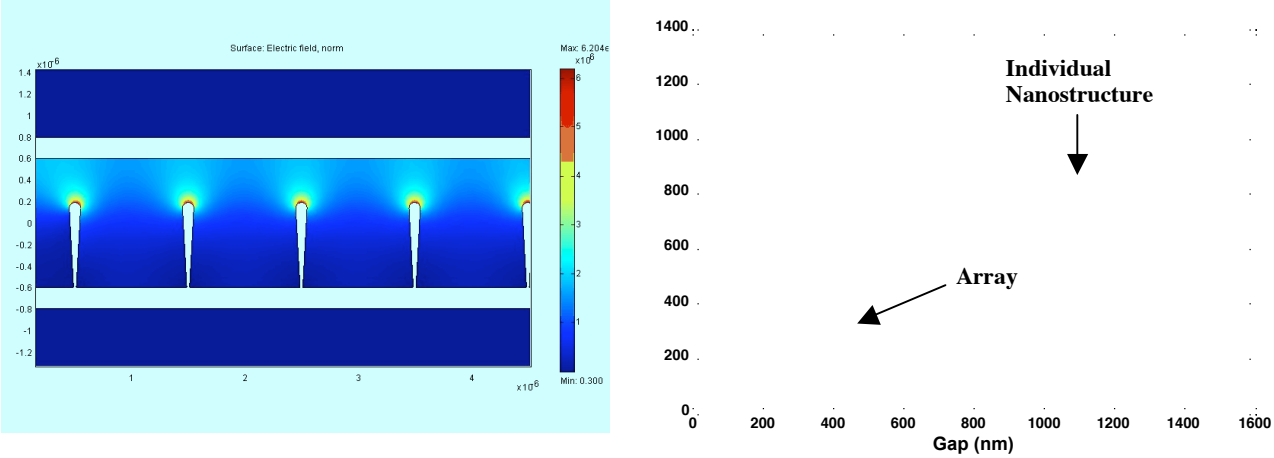

Figure 2: Suppressing field screening in nanostructured electrode arrays. (Left) Simulation of electric field distribution for an array of tungsten nanorods. The electrode gap is varied in the 50-1500 nm range. (Right) Field enhancement factor plotted as a function of electrode gap for both an individual nanostructure and the array. For small gaps the electric field of the array matches that of the individual nanostructure (i.e. the screening is suppressed).

An important aspect of our work is to model the electric field distribution near the sharp nanostructure tips and to study the field-induced interaction of various gas species with the nanostructure tip. Typically for nanostructured arrays, the maximum field that can be generated at the nanostructure tip is limited by the nanostructure's proximity to its nearest neighbor. This phenomenon is called electrostatic shielding or self-screening. The higher the screening (or lower the electric field) the more power is needed to ionize and detect the gas species. Therefore to maximize the efficiency of the sensor devices it is important to alleviate screening.

For nanostructured arrays it is difficult to alleviate screening since the nanostructures are very densely packed. However in a recent breakthrough we showed [4] that this electrostatic shielding effect can be minimized if the electrode gap (i.e. the anode-to-cathode separation) is reduced to less than the nanostructure-to-nanostructure spacing. This is because if the electrode gap is lower than the nanostructure spacing, the concentration of charge at the nanostructure tip is dominated by the local electrode gap and not by the field penetration depth as is the case for larger electrode gaps. In such cases the electrostatic screening effect can be suppressed (i.e. the field enhancement factor for the array can be engineered to match that of the individual nanostructure as shown in figure 2). In this way the full impact of the electric field amplification effect associated with the nanostructure tip geometry can be taken advantage of.

Over the next several years, we propose to perform simulations using first principles density functional method and classical electrostatics to predict the ionization of several gas species and mixtures in the vicinity of nanostructured electrode tips. The nanostructures that we propose to analyze include both carbon nanotubes as well as Tungsten, Ruthenium and Platinum nano-rods. Experiments are also proposed to validate the theoretical predictions. In particular we propose to test easily ionizable analytes of greatest concern to the health and safety community, such as: hydrocarbons, aromatic compounds, phenols, and distillates in mixtures with air.

The proposed work is intended to answer a number of basic scientific questions. These include- 1) How is the electric field around a sharp nanostructure tip affected by the tip size, shape and how does this impact the ionization of gas species; 2) How is the electric field affected by the nanostructure aspect ratio (length to diameter) and nanostructure packing density; 3) How is the sensor affected by so called sticky molecules that may adsorb to the nanostructure surface and alter the field ionization characteristics; 4) How does the field enhancement factor depend on the anode-to-cathode spacing and the device geometry; 5) Can ballistic transport of ionized gas molecules to the sensing electrode be achieved by tuning the electrode gap; 6) What is the maximum sensitivity of detection (parts per thousand, parts per million or higher) and how is this affected by the device geometry and the anode-to-cathode separation; 7) What is the specificity and the response time of the recognition; 8) What happens when complex molecules such as volatile organic compounds are released in a carrier gas; we want to study different types of carrier gases and the effect of carrier gas concentration; 9) It is important to investigate sensor durability by studying impact of cathode sputtering, tip damage and reactive reaction products and exploring strategies to minimize these effects. An improved understanding of these basic issues is essential for the efficient design and utilization of the proposed nanoscale ionization detectors. The research that we are performing in this NIRT project will answer the balance of these issues.

This work has the potential to result in a new class of compact, field-operable nanoscale ionization devices that can provide definitive identification of a range of gas species in real-time mode and at a practically useful level of sensitivity.

References

[1] For further information about this project link to **<www.rpi.edu/~koratn>** or email **<koratn@rpi.edu>**
[2] J. P. Singh, N. Koratkar, T. Karabacak, T.-M. Lu and G.-C. Wang, "Field ionization of argon using β-phase W nanorods," Applied Physics Letters, Vol. 85, No. 15, pp. 3226-3228, (2004).
[3] A. Modi, N. Koratkar, E. Lass, B. Wei and P. Ajayan, "Miniaturized gas ionization sensors using carbon nanotubes", Nature, Vol. 424, pp. 171-174, (2003).
[4] Z. Wang and N. Koratkar, "Suppressing electrostatic screening in nanostructured electrode arrays", Submitted to Nanotechnology- under review, (2005).