Nanoparticle Based Detection

High Sensitivity and Selectivity

Overview

Thin films composed of nanoparticles have emerged as useful chemical sensor platforms. These detection sensors have demonstrated the ability to sense various chemical agents with sensitivity in the sub part per million volume range. Nanoparticle based sensors provide a simple signal transduction scheme based on changes in resistance. They also consume less energy and are easier to integrate into an embedded single chip platform.

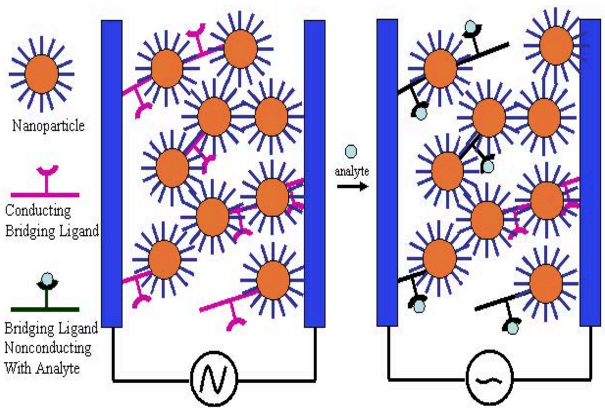

Figure 1. Novel NOM detector.

For this approach metallic nanoparticles are used as a scaffold to support engineered conducting molecular ligands. These ligands are much like short oligiomers of conducting polymers. When an analyte binds to the sensing ligand, the conductivity of the molecule will be altered. To measure the binding event only requires a simple resistance measurement (Figure 1). Components required for the detector include organic sensing molecules *(Conjugated phenylene ethynylene)* (Figure 2) Metal Nanoparticles *(Sacrificial ligands to stabilize in solution and Assembly Techniques)*, and Nano/Micro Gaps.

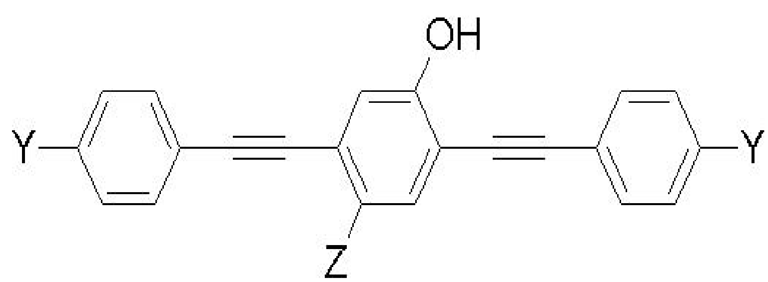

Figure 2. Organic sensing molecules (conjugated phenylene ethynylene).

To engineer a change in the conductivity of the bridging ligand we chose to incorporate hydrogen bonding moieties into a conjugated phenylene ethynylene backbone. When an analyte hydrogen-bonds with our sensing molecule, the molecular orbitals will be altered. Changes in the electron density at the phenol based on the hydrogen bonding can dramatically affect the molecular orbitals of the bridging ligand. Molecular orbital calculations and experiments have shown that increased hydrogen bonding increases the conductivity of the bridging ligand (Figure 3).

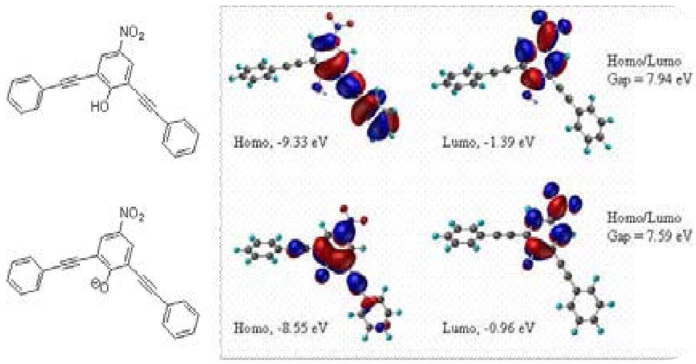

Figure 3. Difference in Homo/Lumo Gaps = 0.35 eV (*14 X kT at RT*).

One of the initial approaches to modulating the sensitivity of the nanoparticle / organic array was to vary the number of different paths available for the electron to travel from one electrode to the other. The use of nanogaps of varying edge length can potentially increase the sensitivity of the film. Towards this goal the fabricating of nanogaps that are amenable to mass production is necessary for the development of the Organic/nanoparticle-film based sensors. Sandia has developed a novel fabrication technique for producing arrays of silicon one dimensional nanogaps based on standard optical lithography and CMOS processing. The process allows for the accurate mass fabrication of gaps in a range from 2-100 nm, making it a useful platform to measure the electrical transduction of organic/nanoparticle films suspended between the electrode gaps. This method generates 1-D nanogaps with silicon electrodes, thereby avoiding metal filament formation. Sandia has fabricated a simple Si 1-D nanogap platform for monitoring the electrical behavior of nanoparticle films. The 7nm gap device showed considerable increase in current after it was functionalized with an organic/gold nanoparticle film.

After functionalization of the surface using diazonium chemistry, an iterative film assembly approach was employed to build the films layer by layer using anternation solutions of the bridging ligands and nanoparticles (Figure 4).

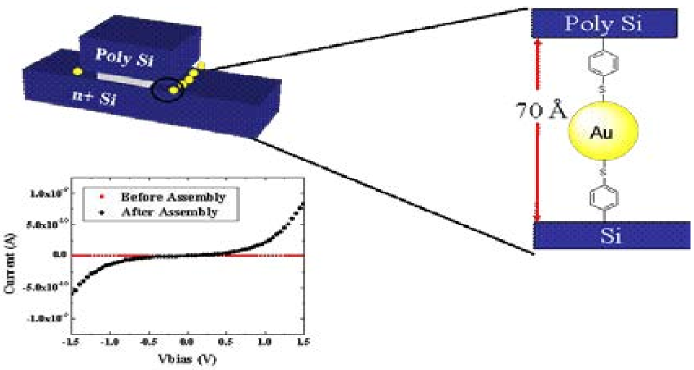

Figure 4. Small gap fabricated from highly dope silicon that can be functionalized via diazonium chemistry.

Sandia has worked on the synthesis of nanoparticles that have a weakly bounded capping agent that is strong enough to prevent agglomeration and in the case of the platinum particles allow for purification, but yet, easily displaced by other strongly binding ligands. While others have displaced ligands on nanoparticles our approach also for the substitution to occur vary rapidly, thus enabling the formation of thick films in a relatively short time. We have accomplished the first synthesis of stable nitrile capped nanoparticles by modification of the Brust method. The nitrile capping agent serves as a sacrificial layer which may easily be replaced by stronger binding ligands *(e.g. thiol, isonitrile or diazonium groups)* (Figure 5). Stearonitile capped Au nanoparticles were assembled in a stepwise fashion onto a Au electrode (Figures 6 & 7).

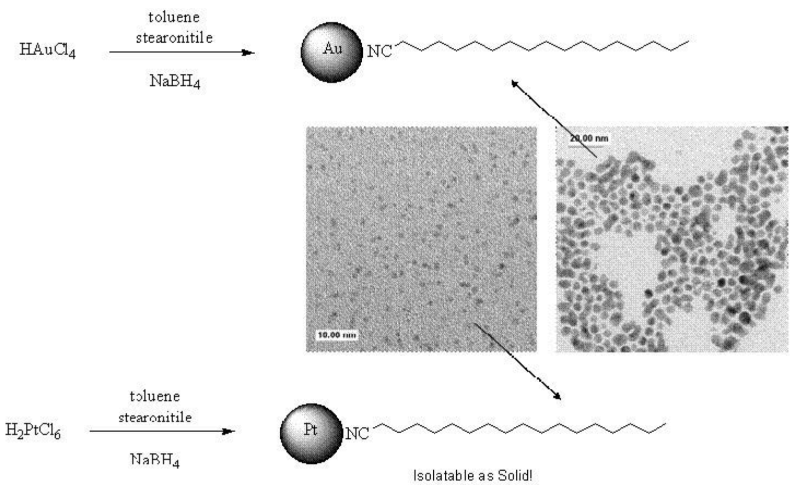

Figure 5. The first synthesis of stable nitrile capped nanoparticles by modification of the Brust method.

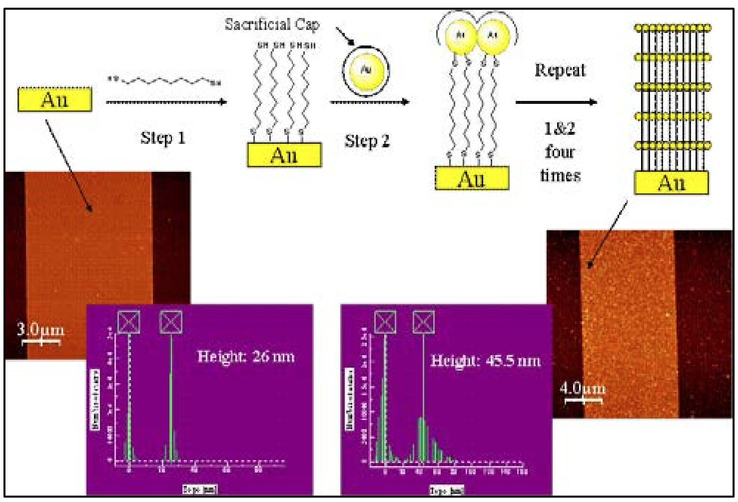

Figure 6. Stearonitile capped Au nanoparticles were assembled in a stepwise fashion onto a Au electrode.

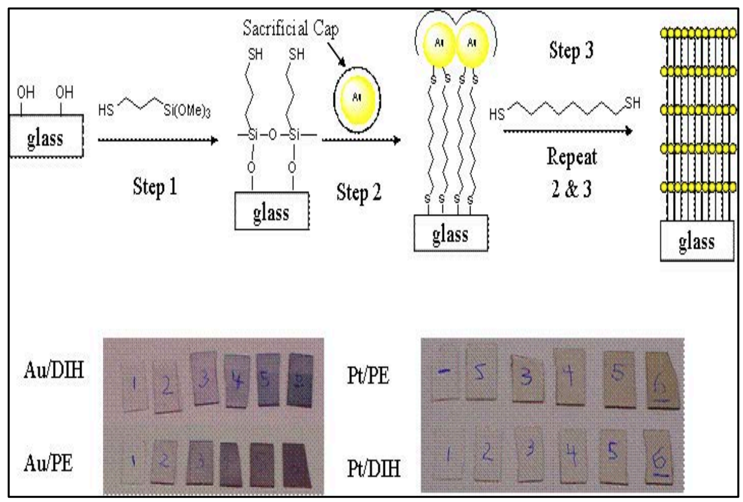

Figure 7. Stearonitile capped Au nanoparticles were assembled in a stepwise fashion onto a Au electrode.

The first observations of molecular switching were in aqueous solution and can be seen in Figure 8. The data shows conductance modifications for a nanoparticle film crosslinked with nitrophenol phenylene ethynylene. During exposure to a base solution, the proton is removed from the phenol, the sensing portion of the molecule. This causes a reduction in film current. Exposing the film to acid restores the H, increasing the film's conduction. This modification was found to be reversible. In Figure 9 this data shows different responses caused by exposures to numerous vapors.

The film comparison plot shows the difference in the behavior of nanoparticle films assembled with sensing and control molecules. While the film linked with the sensing molecule shows a permanent modification to the conduction after cycling, the experiment demonstrates proof of concept. The origin of the hysterisis is understood and relates to the stability of the bridging molecule in aqueous solution.

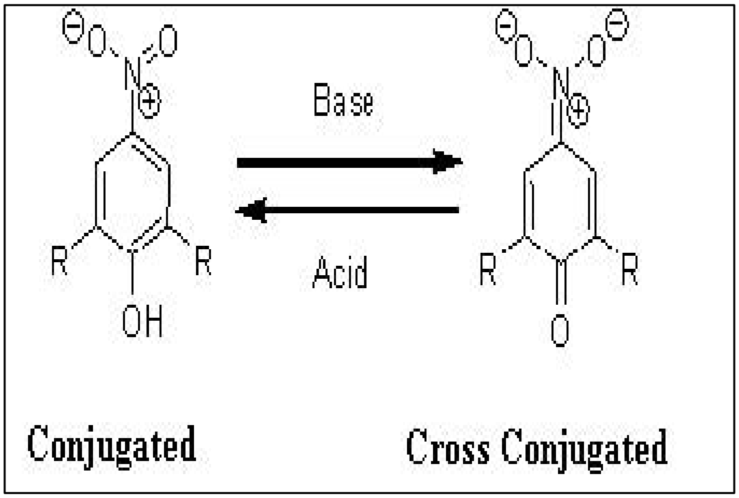

Figure 8. First observations of molecular switching (*liquid phase).*

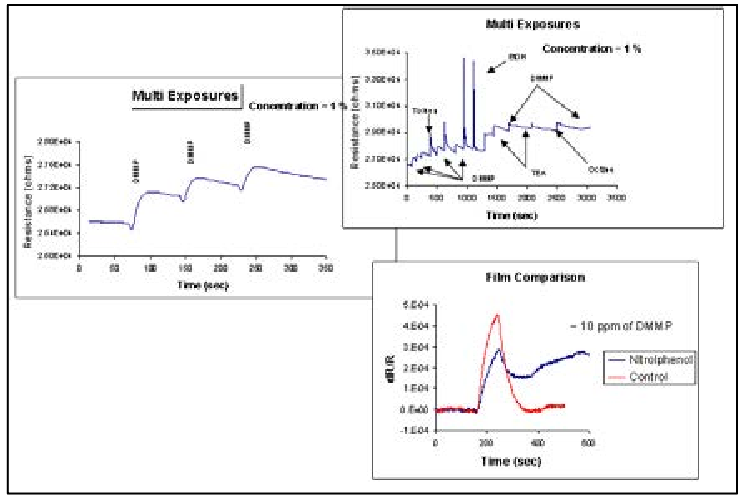

Figure 9. Initial vapor sensing.

Sandia has developed a sample preparation system that enables very reproducible deposition of cross-linked nanoparticle films on a variety of substrates (Figure 10). Use of such a sample preparation system is vital for developing mass-produced sensors from nanoparticle films and gathering statistics on device performance. Data collected for several nanoparticle film depositions demonstrates Sandia's ability to vary the conduction of the organic molecule and thus the total conduction of the film by the judicious selection of nanoparticle size, composition, and the cross-linking ligand. By preparing the nanoparticle films using a robot, problems associated with irregularities of the deposited films are eliminated. This sample preparation system was designed with the capability to measure the resistivity of the nanoparticle films after assembly of each layer. Sandia uses a unique chemistry in conjunction with a robotic sample preparation system to deposit nanoparticle films of different thickness on prepared electrodes in a very reproducible manner. Sandia is currently working on developing complimentary signal transduction methods that may provide more information about the analyte via specific interactions with the organic portions of the nanoparticle network.

Figure 10. Sample preparation system.

One form of detection is the Nanoparticle Organic Molecule (NOM), which is specifically designed to be sensitive to chemical warfare agents. This device consists of an assembly of short organic oligomers and metal nanoparticles.

For additional information or questions, please email us at BioNano@sandia.gov

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2009-1553 W