



Nanoparticle Synthesis For Chemical Detection

HIGH SENSITIVITY AND SELECTIVITY

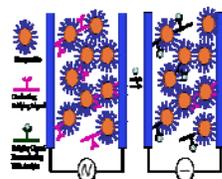
Overview

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.

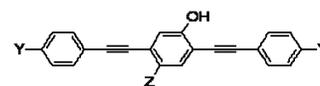
For this approach, metallic nanoparticles are used as a scaffold to support engineered conducting molecular ligands. These ligands are much like short oligomers of conducting polymers. When an analyte binds to the sensing ligand, the conductivity of the molecule will be altered. To measure the binding event only requires a simple resistance measurement. (see picture 1) Components required for the detector include organic sensing molecules (conjugated phenylene ethynylene) (see picture 2), metal nanoparticles, and nano/micro gaps.

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. (see picture 3)

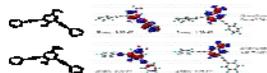
One of the initial approaches to modulating the sensitivity of the nanoparticle / organic array was to vary the number of different paths available for the electron to travel from one electrode to the other. The use of nanogaps of varying edge length can potentially increase the sensitivity of the film. 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



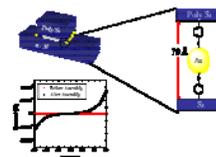
[Novel NOM Detector](#)



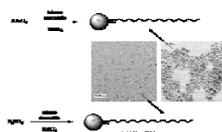
[Organic Sensing Molecules](#)



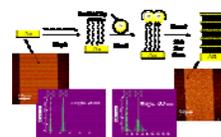
[Homo/Lumo Gaps](#)



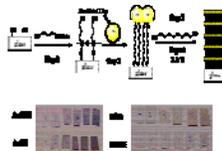
[Small Gap](#)



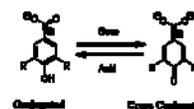
[Nitrile Capped Nanoparticles](#)



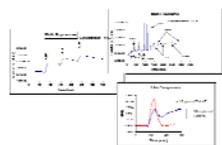
[Au Nanoparticles](#)



[Au Nanoparticles \(Cont.\)](#)



[Molecular Switching](#)



[Initial Vapor Sensing](#)



[Preparation System](#)

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 alternating solutions of the bridging ligands and nanoparticles. (see picture 4)

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). (see picture 5) Stearonitrile capped Au nanoparticles were assembled in a stepwise fashion onto a Au electrode. (see picture 6 and 7)

The first observations of molecular switching were in aqueous solution and can be seen in picture 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 picture 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 hysteresis is understood and relates to the stability of the bridging molecule in aqueous solution.

Sandia has developed a sample preparation system that enables very reproducible deposition of cross-linked nanoparticle films on a variety of substrates. (see picture 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.

Please address comments or questions to BioNano@sandia.gov