

## Modification of Nanoparticle-Organic Composite Electronic Materials for Improved Chemical Sensors

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Molecular electronic based chemical vapor sensors were assembled using noble metal nanoparticles and short conjugated phenylene ethynylene (PE) based molecules. Sacrificial capping ligands on the nanoparticles were replaced by tighter binding PE ligands. The films were assembled between pairs of electrodes by iteratively exposing the substrates to solutions of the nanoparticles and PE crosslinking bridging ligands. Some of the conjugated bridging molecules contained an electron deficient phenol to provide a simple platform for developing sensor applications. The phenol is calculated to have a significant change in its HOMO/LUMO gap in the presence of specific analytes. Judicious combination of nanoparticle size and ligand structure provides a film in which the organic bridging ligands dramatically affect film conductance. Specifically,  $\pi$ -conjugated ligands lower resistance more in films with smaller particles. Thus the sensing mechanism of these films is not based on the typical swelling mechanism but rather on the modulation of the molecular electronic structure of the conducting PE bridging ligands.

Interdigitated Au electrodes built on quartz substrates were first silanized with tetrakis(dimethylamino)silane. The remaining amino functionalities were displaced with 1,8-octanedithiol (ODT) to give a thiolated surface capable of binding nanoparticles. The substrate was then incubated in a solution of dodecylamine-capped nanoparticles. The film thickness was increased via alternating exposure to solutions of bifunctional crosslinking molecules and nanoparticles (Figure 1). Nanoparticles and assembled films were characterized by TEM and AFM prior to electrical characterization.

After verifying the selectivity of this new attachment chemistry, a novel robotic sample preparation was employed to build nanoparticle films of different thickness on prepared electrodes. By preparing the nanoparticle films using a robot, many problems with irregularities of the deposited films were eliminated. This sample preparation system was designed with the capability to measure the resistivity of the nanoparticle films after assembly of each layer. Using such a sample preparation system is vital for developing mass-produced sensors from nanoparticle films.

The robotic system was used to deposit and measure the electrical properties of Pt and Au nanoparticles linked with different ligands such as ODT and meta-PE diisocyanide. Figure 2 is a plot showing the resistance vs. film layer for several combinations of nanoparticles and linker-ligands. The data shows that the resistance of the film drops and eventually saturates as additional nanoparticle layers are deposited. There is also an inversion in the resistance per layer that depends on the nanoparticle's type and the ligand used to crosslink the film. This data is significant because it shows how the selection of certain nanoparticle properties (such as size and material) and selection of an appropriate linking ligand can be used to tune the conductance of a film composed of nanoparticles. It is well known that smaller nanoparticles have a higher charging potential. This coupled with the inherent variability of organic molecules

ensures that a film in which the organic molecules dominate conductivity can be achieved.

In addition to the experiments above, nanoparticle films were assembled using cross-linkers that can be modified by an analyte. Figure 3 shows a typical I(V) curve for a Au nanoparticle film crosslinked with a phenylene ethynylene based electron deficient phenol. There is a clear reversible change in the resistance of the film when exposed first to acid and then base. The generation of a new response mechanism for nanoparticle films greatly increases the scope of organic/nanoparticle films for sensor applications. Their crosslinked nature increases their robustness and allows for use in both aqueous as well as organic solutions.

In summary, we have developed a novel reproducible sample preparation system for the deposition of crosslinked nanoparticle films on a variety of substrates. This system has the ability to acquire electrical data during the sample deposition. Data collected for several nanoparticle film depositions demonstrated the ability to tune the conduction of the film by the selection of nanoparticle size and the cross-linking ligand. The material we have developed is a hybrid intermediate between a true organic conducting polymer and a classical nanoparticle film. The nanoparticles provide a scaffold on which to assemble various conducting/sensing oligomers and ligands without the problems inherent to conducting polymers.

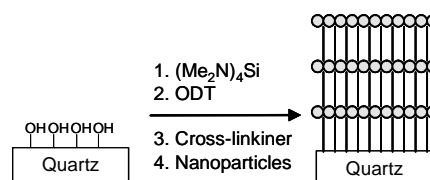


Figure 1 Silanization of quartz substrate and nanoparticle assembly.

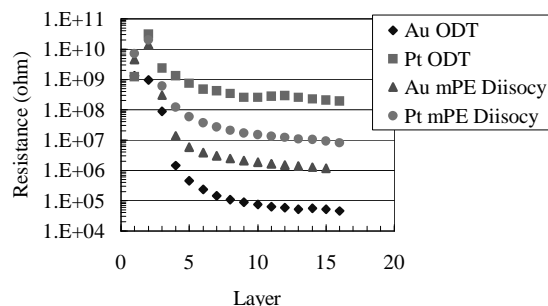


Figure 2 Resistance vs. layer data for several combinations of nanoparticles and linker molecules.

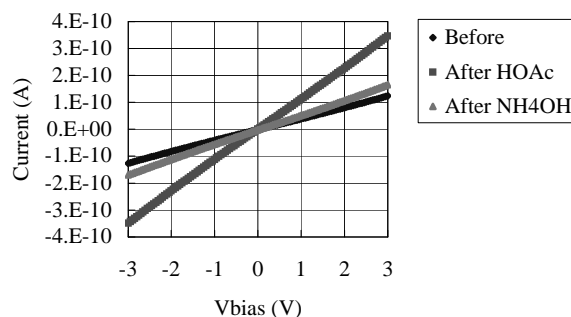


Figure 3 A typical I(V) curve of a nanoparticle film before and after exposure to HOAc and  $NH_4OH$ . There is a reversible change in the resistance of the film.