Chemical Crosslinking and Temperature Dependant Conductivity of Ligand-Stabilized Gold Nanoparticles

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MATERIALS

Abstract:

Inorganic nanoparticles have unique nanoscale optical and electrical properties independent of their bulk systems. This research focused on chemical modifications of gold nanoparticle arrays to manipulate conductivity of films of these nanoparticles. Organic ligand chains attached to nanoparticle cores were crosslinked using dithiols to increase conductivity. The temperature dependant conductivity of nanoparticle films as a function of chemical crosslinking was measured, and it was found that crosslinking ligands enhance conductivity, as does increasing temperature.

Introduction:

The gold nanoparticles (AuNPs) used in this research have an approximate diameter of 2 nm: this particle size determines the single electron charging energies in nanoparticle films and governs the AuNP's electrical properties. It is important to be able to understand, characterize, and model the behavior of gold nanoparticles, especially the electronic properties as a function of chemical modification. With this knowledge, it would be possible to manipulate AuNPs to have well defined, stable properties for use in electronic or semiconductor devices [1].

Experimental Procedure:

In this project, AuNPs were chemically modified in an effort to manipulate the conductivity of their corresponding films as spin-coated on top of electrodes. The nanoparticles were solution synthesized using the Brust method and the gold cores were stabilized with insulating hexane thiolate (C_6) ligands [2]. Nanoparticles were kept in concentrated toluene or heptane solutions (~350 mg NPs/mL solvent). The conductivity of the nanoparticles was measured by making thin AuNP films on electrodes and measuring the resulting current as a voltage was swept across the metal contacts (-4 V to 4 V). Nanoparticle solutions were spin-coated (2000 rpm) into thin films (~300 nm thick) on small electrical devices such as interdigitated electrodes (IDEs) or planar electrodes made in lab. For the planar "sandwich" electrodes, a thin gold film was evaporated on top of the AuNP film to form a top contact. The NP films were crosslinked using dithiols to interlink the AuNP cores and the conductivities of the films were measured at temperatures from 80 to 320 K using a liquid nitrogen vacuum cryostat to control the temperature.

Crosslinking:

The goals of this research were to develop a mathematical model to describe the electrical effects of crosslinking and to understand the mechanisms of charge transport in AuNP films. To crosslink AuNPs via bifunctional organic ligands, the nanoparticle films were submerged in dithiol solutions from 30 minutes up to four hours. Over time, dithiols in solution replaced more of the hexane thiols attached to AuNP cores. Nonanedithiol (NDT) and benzenedithiol (BDT) were used to crosslink ligands in concentrations of 5 μL NDT per mL isopropyl alcohol and 5 μg BDT per mL toluene.

Results and Conclusions:

For IDEs, current-voltage plots always displayed ohmic behavior. Current was a constant function of bias, and conductivity only increased with increasing temperature. Nanoparticle films on sandwich electrodes did not display ohmic behavior after biases much larger than ± 0.2 V were applied, as can be seen in Figure 1. Investigation of this behavior is necessary to understand what mechanism causes this drastic increase in conductivity.

$$\sigma = \sigma_0 \exp\left(-E_A / RT \right)$$

The amount of crosslinking, and thus conductivity, was directly related to the amount of time spent in solution. Data characterizing the temperature dependant nature of this relationship could be fit to an Arrhenius equation where E_A is activation energy, R is the gas constant

(8.3144 J/mol K), and T is the temperature in Kelvin. Low field conductivity data, where the current-voltage relationship remained linear, was fit to this model as can be seen in Figure 2.

Because distinctly different current-voltage relationships were observed at low biases versus those at high biases, the temperature dependant data was divided into low (-0.2 V to 0.2 V) and high (4 V) field conductivity models for analysis. In Figure 2, low field conductivities of the film as uncrosslinked, crosslinked in NDT solution, and crosslinked in BDT solution, were plotted together. The activation energy decreases slightly from the uncrosslinked film (E_A = 15.4 kJ/mol) to NDT crosslinking (E_A = 14.7 kJ/mol), but the significant decrease in activation energy is observed after BDT crosslinking (E_A = 10.5 kJ/mol). The double bonds in the benzene ring in BDT allowed for significantly faster electron transfer, and thus, much higher conductivities were observed. According to the Arrhenius equation, electron hopping is a logarithmic function of temperature, so the conductivity shows extremely strong temperature dependence. The activation energy for an electron to "hop" to an adjacent nanoparticle provided a quantitative parameter to compare the effects of crosslinking.

In Figure 3 it is evident that high field conductivities deviate from the Arrhenius model. To model the high field conductivity behavior, a variable range hopping (VRH) model was used, where electrons were theoretically able to jump more than one AuNP core or "potential well" at a time. As a result, conductivity became a linear function of the square root of inverse temperature, as opposed to only inverse temperature, as in the Arrhenius model.

Future Work:

A comprehensive model for the low and high field conductivity must be verified. The ultimate goal of this nanoparticle characterization is to be able to understand the charge transport mechanisms in order to control electrical AuNP properties. This knowledge could then be applied to solution synthesized semiconductor nanoparticle systems with optoelectronic and photovoltaic applications.

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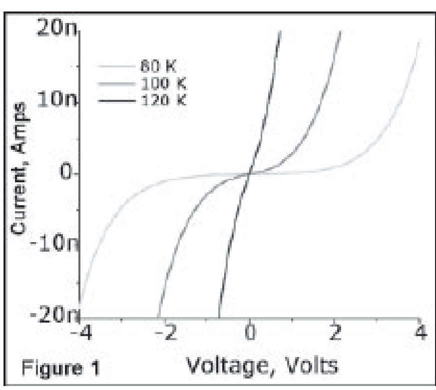

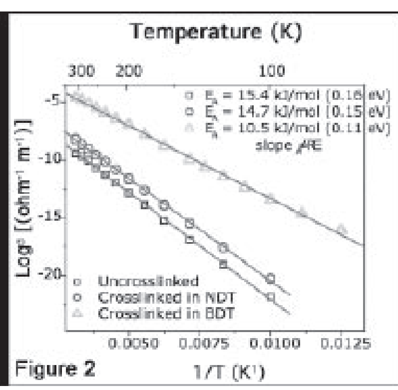

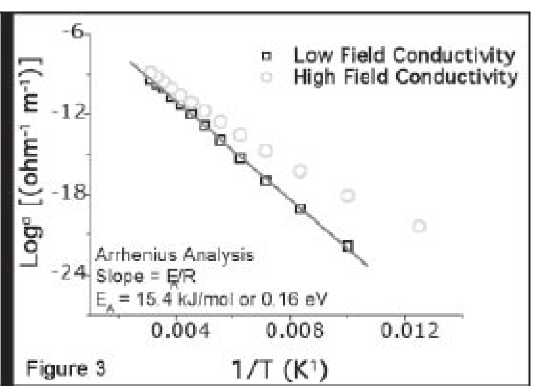

Figure 1: Conductivity of uncrosslinked AuNP film at low temperatures.

Figure 2: Arrhenius analysis of low field conductivity on a sandwich electrode.

Figure 3: Low and high field conductivity of an uncrosslinked film.