Charge Transport in Gold Nanocrystal Arrays

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Abstract

This research focused on gold nanoparticles, and the single electron charging of these nanoparticles as a function of electrochemical potential. We have synthesized a variety of gold nanoparticles, processed them into thin films, and tested these films with cyclic voltammetry (CV) and dual electrode voltammetry (DEV). We have also begun to look at the effect of temperature on the conductivity. We found that conductivity is related to the electrochemical potential applied to the film as well as temperature.

Introduction

Metal nanoparticles have scientific importance because their electronic properties depend on size, shape and composition. Due to this, these properties can be controlled and manipulated [1]. It is important to understand this phenomenon in order to fabricate devices that utilize these properties. Gold nanoparticles have been studied previously, and the synthesis of purportedly monodisperse particles has been reported [2]. We optimized our synthesis such that the average diameter of our nanoparticles was 2.0±0.6 nm. The size of the nanoparticles is what governs the charging, and this size distribution was narrow enough to give reproducible electrochemical data.

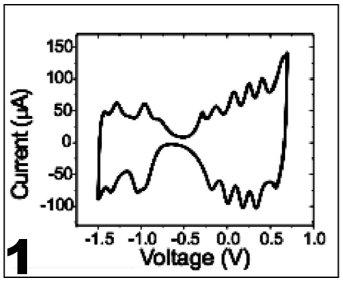

Figure 1: Cyclic voltammetry data.

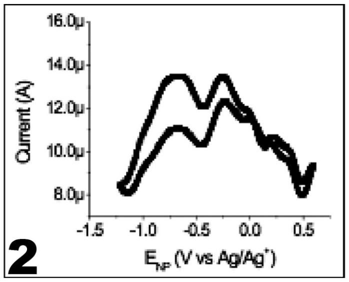

Figure 2: Dual electrode voltammetry data.

Experimental Procedure

Gold nanoparticles were synthesized using a modified Brust method [3], with hexanethiol as the stabilizing alkanethiol ligand. After the reduction reaction was complete, ethanol was added and the ethanol-soluble particles were isolated. Concentrated solutions (~ 250 mg/ml) were prepared in heptane, and thin films were spin-coated (2000 rpm) onto platinum electrodes. For DEV, gold was evaporated on top of the nanoparticle film so that conductivity could be measured through the film. All films were cross-linked in 1,9-nonanedithiol before running CV and DEV.

CV was run under argon, with tetrabutylammonium hexafluorophosphate as the electrolyte in acetonitrile. The reference electrode was Ag/Ag^+, and the counter electrode was platinum wire. DEV was conducted under the same conditions as CV. Temperature dependence studies were carried out in a cryostat to allow measurements under vacuum and down to liquid nitrogen temperature (77 K).

Results and Discussion

Gold nanoparticles exhibit discrete charging energies and this can be seen on the CV graph (Figure 1). Each peak relates to a single electron charging of half of the nanoparticles, on average. This is an average because the particles aren't all exactly the same size. At the valleys in between the peaks, all the nanoparticles are filled with electrons to the same energy level. At this potential, electron tunneling can only occur if there is thermal activation of an electron to a higher energy level. At the potentials that relate to peaks in the CV graph, electron tunneling can occur without thermal activation since half the nanoparticles already have an electron in a higher energy level. This would mean an increase in conductivity at those specific potentials.

In order to analyze the conductivity as a function of the charge on the nanoparticles, we tested our films with DEV. Figure 2 is the data from the DEV experiment, where conductivity is plotted as a function of potential. From what we know about the CV data, this potential can also be thought of as the charge potential of the nanoparticles (E_{NP}). The peaks in the DEV graph occur at similar potentials as the peaks in the CV graph. This supports the claim

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

σ_0 = constant
E_A = activation energy
R = gas constant
T = temperature

Figure 3: Arrhenius equation describes thermal activation at low biases.

that these potentials relate to charging of half the nanoparticles, because this data shows that there is an increase in conductivity at these potentials.

Temperature Dependence

To more fully understand the mechanism of electron tunneling, it is helpful to analyze the effect of temperature. It is also a way of validating the claim that there isn't a need for thermal activation at certain potentials applied to the film. Initially we tested the effect of temperature on conductivity of the uncharged nanoparticle film, to verify that it follows the Arrhenius equation (Figure 3). The Arrhenius equation describes thermal activation of electrons and holds true at low biases. Figure 4 is the temperature dependence data and can be used to calculate the activation energy of an electron. This information would be useful if gold nanoparticles were used in electronic devices.

Conclusion

Cyclic voltammetry is a good method for analyzing the charge on the nanoparticles. In this experiment, we could detect the addition of a single electron to the nanoparticles by observing a peak. This data matched up with conductivity measurements, since there were peaks in conductivity at nearly the same potentials as the peaks in the CV graph. This is what we would expect because of the lower barrier for electron tunneling when half the nanoparticles are charged. Temperature is related to conductivity by the Arrhenius equation, and we observe this when we measure conductivity at various temperatures.

Future Work

The next step will be to combine the DEV study with the temperature dependence study. This means driving to the potentials that relate to peaks in the DEV and then running the temperature dependence experiments. This would be a way to confirm the hypothesis that there is little to no thermal barrier for electron tunneling at these potentials. Another experiment would be to vary the electrolyte used for CV and DEV, to see the effect of ion size on the charging of the particles.

Acknowledgements

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References

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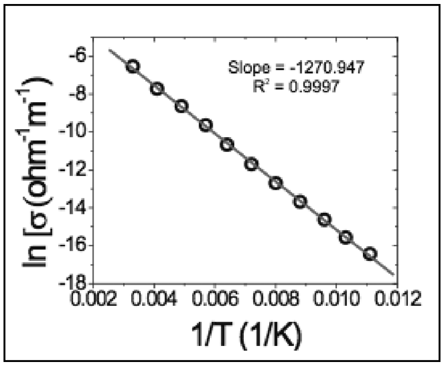

Figure 4: Temperature dependence data; from Arrhenius equation, slope = E_A/R, E_A = 0.110 eV.