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Anisotropic Nanoparticles— Synthesis, Characterization and Applications

EDITORS

L. Andrew Lyon
Stephan J. Stranick
Christine Dolan Keating
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Anisotropic Nanoparticles— Synthesis, Characterization and Applications

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**Anisotropic Nanoparticles—
Synthesis, Characterization
and Applications**

PREFACE

This volume contains a series of papers originally presented at Symposium C, "Anisotropic Nanoparticles—Synthesis, Characterization and Applications," at the 2000 MRS Fall Meeting in Boston, Massachusetts. In addition to support from the Materials Research Society, this symposium was co-sponsored by NIST, NSF-DMR, and ONR, with corporate support from SurroMed, Inc. and Digital Instruments.

The purpose of this symposium was to review the broad multidisciplinary activities in this rapidly growing area. The properties of nanoscale materials are derived from the additional dimensional and compositional degrees of freedom that arise when the physical dimensions of the system are smaller than a characteristic length scale of interest. Anisotropic particles can exhibit novel and enhanced properties compared to isotropic spherical particles. This symposium focused on all aspects of anisotropy on the nanoscale, including anisotropy resulting from shape (e.g. rods, nanowires, biomolecules), juxtaposition of different materials (e.g. nanoparticle heterodimers), compositional heterogeneity (e.g. core-shell particles, multilayer nanowires) or the intrinsic directionality of a probe (e.g. electromagnetism).

In addition to the synthesis of new anisotropic materials, the ability to address individual nanostructures (e.g. electrically, magnetically, or optically) is important for technological applications such as nanoelectronics and biomedical engineering. Furthermore, the assembly of ordered 1D, 2D, and 3D arrays of anisotropic nanoparticles presents new challenges not encountered with isotropic particles. Chemical interactions (e.g. self-assembly) and electric fields (e.g. electrostatic trapping) can be used to assemble ordered arrays from colloidal suspensions. The ability to address isolated anisotropic particles (e.g. nanowires, DNA strands) allows fundamental measurements of properties such as electrical transport and tunneling. By assembling an extremely multidisciplinary group of scientists, this symposium attempted to address all of these issues in some way. This volume presents a subset of the presentations in this symposium and attempts to provide the scientific community with a progress report in nanoscale anisotropy and its applications in a variety of fields.

L. Andrew Lyon
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April 2001

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*Invited Paper

Structure and Electrical Properties of an Assembly of Au Nanoclusters

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Oak Ridge, TN-37831-6123.

ABSTRACT

Conduction through an assembly of nanosized clusters coupled by tunneling barriers is of significant interest both for understanding the fundamental physics involved and for potential applications. In this study, we describe a technique for preparing relatively large (dimensions of a few 100 μm to a few mm in size) monolayer films consisting of 3 nm diameter Au clusters coated with mercaptododecanoic acid, using low molecular weight-polymers as coupling agents. Electrical measurements of the assembly show non-linear characteristics. Below a certain threshold voltage, the current does not vary with an increase in voltage. Above this threshold voltage, current increases with voltage and can be described by a power-law relationship with an exponent close to unity. These characteristics of the I-V curve are discussed with specific reference to theoretical studies on conduction through an array of capacitance-coupled metallic islands and previous experimental results in similar systems.

INTRODUCTION

Recently, there has been significant interest in observing Coulomb blockade effects at room temperature in systems containing multiple tunnel junctions comprising of small, metallic clusters separated by tunnel barriers due to potential applications in nanoscale electronics [1-5]. Two criteria have to be satisfied for observing Coulomb blockade in such systems. Firstly, the Coulomb charging energy of the cluster or island ($E_c = e^2/2C$) where e is the electron charge and C is the capacitance of the island, has to be larger than the ambient thermal energy kT . The second criterion to be satisfied is that the tunnel barrier between islands must have a tunnel resistance greater than the quantum resistance h/e^2 , where h is the Planck's constant. Ligand-stabilized metal particles offer an attractive method for synthesizing two-dimensional arrays of multiple tunnel junctions, since the ligand shells not only facilitate coupling amongst the metallic clusters but they also serve as tunnel barriers [6].

Various methods have been used to synthesize two-dimensional assemblies consisting of nm sized metallic clusters separated by ligand shells. Spin casting has been used to prepare ordered assemblies of size 450 nm consisting of 3.7 nm Au clusters [2, 7]. Biopolymer templates have been used to prepare two-dimensional assemblies consisting of 0.7 nm Au nanoparticles between electrodes separated by distances of 15 μm [3-5]. Room temperature electrical conductance of such an assembly showed evidence of Coulomb gap. In the current study, we present a methodology to prepare relatively large assemblies (100 μm – 2 mm in size) consisting of Au clusters coated with mercaptododecanoic acid. We also present room temperature electrical properties of such assemblies, which show evidence of a Coulomb gap.

EXPERIMENTAL METHOD

Au clusters coated with mercaptododecanoic acid were obtained by a modification of the given by Zhao and Crooks [8] which involves the use of polyamido dendrimers and electroless

displacement of a copper metal colloid by Au (III) ions. The reaction was conducted in 30mL of a 2:1 mixture of water and tetrahydrofuran. The insoluble product was extracted with toluene and centrifuged to obtain reddish gold colloids. Films were observed to form at the liquid-vapor interface after reaction mixtures containing the carboxylic acid-coated gold colloids and equivalent amounts of polyethyleneimine were stirred for a few minutes. The films were seen clearly as a reflective coating on the surface and could be isolated as platelets of sizes ranging from a few hundred microns to as large as 1-2 mm on each side. In some instances, peptide linkages between the acid and the polymer were made through the intervention of EDC by itself or through an intermediate step involving the use of N-Hydroxysuccinimide, NHS, to modify the carboxylic acid into an amine reactive NHS ester. Further details of the preparation of the clusters and the films may be obtained from [9].

Au clusters were characterized by x-ray diffraction (XRD) to confirm crystallinity and to derive an average crystallite size. After washing them thoroughly to remove the reaction medium, infrared spectra were obtained from the colloids to assess the local molecular environment that enabled the association of the colloidal clusters. Gold cluster sizes and spatial organization of the clusters within the films were characterized using transmission electron microscopy (TEM) of the films placed directly on coated copper grids. Atomic force microscopy was also performed on both the individual Au clusters and the films. For the AFM study, individual Au clusters were suspended in water or methanol and a drop of the solution was dispensed and spin-coated on mica. The free-standing films were characterized by allowing them to settle on a sapphire substrate. For electrical property measurements, the films were collected on a pyrex or a sapphire substrate and electrical contacts were made to the films using silver paint. I-V characteristics were measured in an electrically isolated Faraday cage under controlled low-humidity conditions.

RESULTS

Figure 1 shows an XRD pattern from the clusters coated with mercaptododecanoic acid. The x-ray diffraction pattern shows that the particles are crystalline with the presence of Au (111), (200) and (220) lines. Note that, as expected, the peaks show significant broadening due to the size of the particles. Scherrer analysis of the peaks results in particle sizes of about 3 nm. Figure 2 shows the TEM image obtained by evaporating a droplet of the liquid containing the Au colloids mixed with polyethyleneimine and carbodiimide on a carbon-coated Cu grid. The sizes of the clusters observed in the TEM are consistent with the results of the XRD analysis. Note that there is a significant tendency for the clusters to associate into small assemblies with the overall shape of the assembly being circular. From the figure, it should also be observed that there is very little overlap in the images of the clusters within a group indicating that these prefer to form monolayers (2-D structures) rather than to associate to form a three-dimensional assembly.

Figure 3 shows an AFM image obtained from a mica surface on which the Au clusters were dispersed by spin coating a suspension consisting only of the clusters in water and without any coupling agents. The images were obtained using the tapping mode with very low tapping force. As observed from the figure, there is decreased tendency for the particles to associate under these conditions, clearly illustrating the role of the coupling agents in inducing the assembly of the clusters shown in figure 2. Figure 4 shows the variation in height obtained along the specified line shown in the figure. AFM imaging shows a typical height of 1.7 nm for the clusters, which is smaller than that predicted by both analyses of the x-ray data and electron

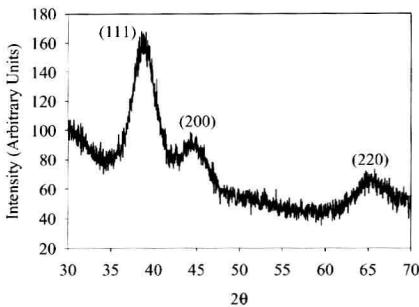


Figure 1. X-ray diffraction pattern from the Au clusters coated with mercaptododecanoic acid.

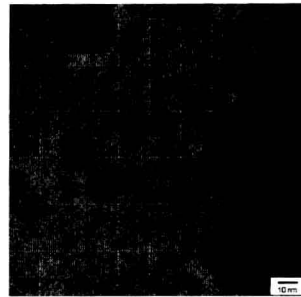


Figure 2. TEM micrograph of evaporation residue from liquid containing Au clusters mixed with polyethyleneimine and reaction promoted with carbodiimide.

microscopy. It is possible that the AFM image shows a smaller particle size due to tip-induced deformation of the clusters. Further experiments are underway to confirm this hypothesis.

Figure 5 shows a TEM image of a film collected on a carbon-coated TEM grid. Note the presence of a space-filling arrangement of the Au clusters. Although no defects are observed in the film over the scale of a few hundred nm, small regions devoid of clusters have been observed when imaging is performed over the scale of a few microns. An important feature to note from this image is that the inter-cluster spacing is not always uniform and the structure does not seem

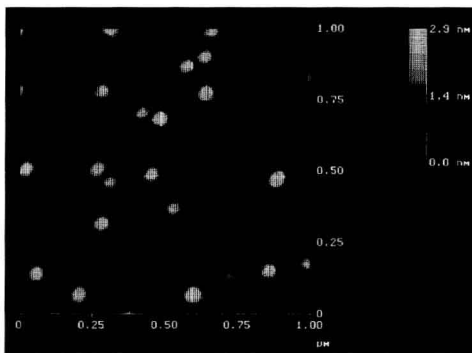


Figure 3. Tapping mode AFM image of the Au clusters dispersed on mica.

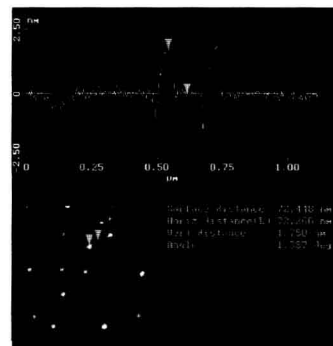


Figure 4. Variation in height obtained from the AFM image shown in figure 3 and along the trace shown in the figure.

to show any long-range order in the organization of the individual clusters.

Figure 6 shows an optical microscope image of a film that was collected on the surface of a sapphire substrate. Electrical connections were made to the film using Ag paint. Also shown in the figure are the two electrical contacts with the distance of separation measured to be $220\ \mu\text{m}$. Figures 7 and 8 show the I-V characteristics of the film shown in figure 6 for two different ranges of voltages. Figure 7 shows the measured I-V characteristics (linear scale), both in the presence and in the absence of the film, for the voltage range of 0.01 to 1 volt with an incremental voltage of 10 mV. To measure the I-V characteristics in the absence of the film, the film was mechanically removed from the substrate without disturbing the two Ag contacts. Clearly, in the presence of the film, the observed current for a particular voltage is larger than that observed in the absence of the film. This confirms the role of the film in the electrical conduction between the two contacts. Also note that the minimum measurable current between the two contacts is of the order of a few fA. Figure 8 shows the current-voltage response (log-log scale) of the film over the voltage range of 0.01 to 30 V. An important feature of the curve shown in figure 8 is that it is not linear. It should be noted that in the voltage range 0.01 to 0.1 V, the current does not increase significantly with an increase in voltage. This can be seen in both figures 7 and 8, although more dramatically in figure 8. Note further that for voltages greater than about 1.0 volt, the $\log(I) - \log(V)$ curve is linear with a slope close to unity. The non-linearity in the I-V characteristics of the film indicates that the presence of the tunnel junctions has a significant impact on the conductance through this film [10].

DISCUSSION

Electrical transport through the disordered array of Au clusters used in this study shows some of the characteristics predicted by the theoretical models and is consistent with previous experimental work. Middleton and Wingreen [10] studied conduction through a one and a two-dimensional array of small capacitance-coupled metal dots with charges allowed to tunnel between neighboring dots. Based on this model, they predicted that onset of conduction through

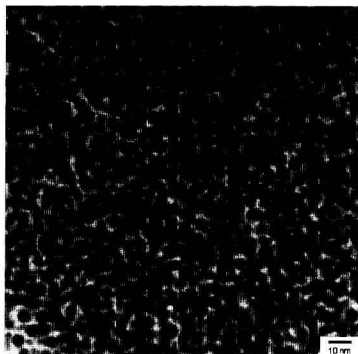


Figure 5. TEM image of the film formed by the assembly of the Au clusters.

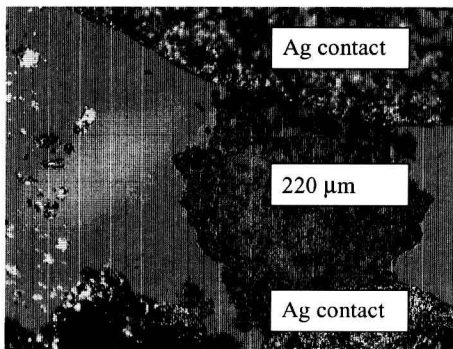


Figure 6. Optical micrograph of a film used for electrical measurements. The film was collected on a sapphire substrate.

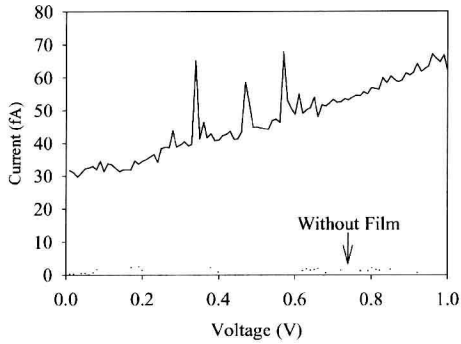


Figure 7. I-V characteristics obtained from the film shown in figure 6 for the voltage range 0.01 to 1.0 V. Also shown in the figure is the current observed between the contacts in the absence of the film.

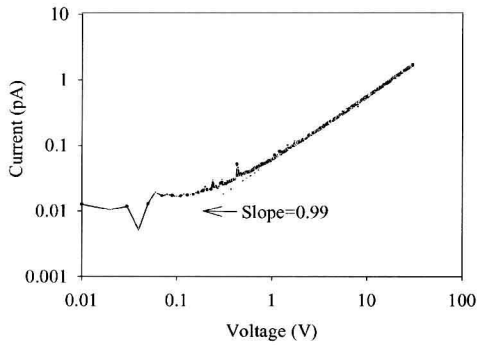


Figure 8. I-V characteristics obtained from the same film over the voltage range of 0.01 to 30V (log-log scale).

the array would occur at a threshold voltage V_T which is proportional to its linear size. Further, they predicted that above the threshold voltage, the current through the linear and square array would vary as