Fabrication and electrical transport characteristics of low-dimensional nanoparticle arrays organized by biomolecular scaffolds

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We report the use of a biopolymer scaffold in the nanofabrication of low-dimensional arrays of gold nanoparticles. The room-temperature current-voltage dependence shows threshold behavior characteristic of Coulomb-blockade. Above threshold the current varies linearly with voltage which suggests one-dimensional behavior. Capacitance estimates are consistent with transport through a disordered chain containing a minimum of 200 nanoparticles.

1. INTRODUCTION

Ligand-stabilized metal nanoparticle systems offer an attractive route towards Coulomb-blockade devices that operate at room temperature. Metal nanoparticles are advantageous for several reasons. First, their size yields a low intrinsic capacitance, thus a high charging energy; second, the stabilizing ligand shell can be used as a tunnel barrier between metal cores with a tunneling resistance much larger than h/e^2; finally, the ligand shell can be used to immobilize the nanoparticle. Forming well-defined structures and architectures from metal nanoparticles present significant challenges. Several approaches have been reported, including the self-assembly of large two-dimensional arrays and the deposition of nanoparticles onto prefabricated electrodes [1,2]. In this paper we discuss a nanofabrication method that involves the assembly of 11-mercaptoundecanoic acid stabilized gold nanoparticles onto the biopolymer poly-L-lysine which acts as a scaffold or template [3]. The metal core is predominately Au_{55} and has a radius $R = 0.7$ nm. The radius of the nanoparticle including the ligand shell is $r = 2.1$ nm. Decorating the scaffold with nanoparticles is accomplished via the attachment of the ligand-shell acid group to the amine side chain of the biopolymer. The current-voltage (I-V) characteristics of samples assembled in this way show Coulomb-blockade characteristics at room temperature. When compared with other nanoparticle systems prepared without the biopolymer, the current-voltage scaling suggests that the poly-L-lysine facilitates one-dimensional chain formation.

2. EXPERIMENT

The poly-L-lysine 11-mercaptoundecanoic acid stabilized Au_{55} nanoparticle system was fabricated on an interdigitated electrode arrangement of spacing 15 μm deposited on glass. First, a 2.2×10^{-5} mol/l solution of poly-L-lysine-hydrobromide complex in 10/90% water/methanol was drop cast onto the carefully cleaned electrodes. From the molecular weight the average length of the poly-L-lysine was estimated to be 30 nm. The hydrobromide was removed from the amine side chains of the poly-L-lysine by submerging the cast film in a solution of 1% sodium hydroxide in water for about 20 hr. The 11-mercaptoundecanoic acid stabilized gold nanoparticles were synthesized from $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$ using ligand exchange [4]. A concentrated solution of the nanoparticle in dimethylsulfoxide was put on the poly-L-lysine film for about 20 min., after which it was rinsed in dimethylsulfoxide followed by dichloromethane. The sample was finally dried in nitrogen. Current-voltage measurements were made in a shielded vacuum chamber at room temperature [3]. The current resolution was 10 fA and the intrinsic leakage of the interdigitated electrodes set the minimum resolvable conductance to be about 4×10^{-15} Ω^{-1}. Control measurements were made at several stages of sample preparation to determine the functional form and magnitude of the background current. Experiments to determine sample stability, the effect of non-specific nanoparticle binding and behavior in the presence of an external radio frequency signal will be reported elsewhere.

3. RESULTS AND DISCUSSION

A representative I-V characteristic of the biopolymer-nanoparticle sample is shown in Figure 1. Below a threshold of 34 ± 5 V the measured current is indistinguishable from the leakage current of the electrodes themselves. Above threshold the slope of the characteristic is close to unity, as seen clearly by the reduced voltage plot in Figure 2. Linear I-V behavior above threshold is expected for both ordered and disordered one-dimensional Coulomb-blockade systems [5,6]. For comparison, in Figures 1 and 2 we also show a typical I-V characteristic of a ligand-stabilized Au_{55} film prepared by drop casting [3]. The similarity in threshold voltage between the two data sets is not significant; the thin film data was chosen to have a comparable threshold voltage. Of importance is the fact that the comparison data has a close to quadratic voltage behavior above threshold, which we have found to be typical for a variety of thin Au_{55} containing films [3].

To model the structure we assume a close packed arrangement of ligand-stabilized nanoparticles attached to the biopolymer. The average length of the biopolymer and the nanoparticle radius suggests that seven nanoparticles decorate each polymer unit. We also assume that each nanoparticle is capacitively coupled to its nearest neighbors and to a ground plane. Modeling the inter-nanoparticle capacitance, C, as the capacitance between two spheres of radius R separated by a distance $2r$, and taking the dielectric constant of the ligand shell material to be 3, we obtain $C \approx 4 \times 10^{-2}$ aF. Because the substrate is glass and the sample is between widely spaced electrodes, the dominant term in the capacitance to ground is $C_g \approx \varepsilon R = 2 \times 10^{-1}$ aF, thus $C/C_g \approx 0.2$. With this capacitance ratio it is not possible to explain the high threshold voltage in terms of an ordered one-dimensional array [7]; a model that includes disorder is required [6,8]. The threshold voltage of an array with a uniform distribution of offset charges from $-e/2$ to $e/2$ is given by $V_T C_g / eN = \alpha(C/C_g)$, where N is the number of nanoparticles in the array and e is the charge quantum. $\alpha(0.2) \approx 0.2$, thus we
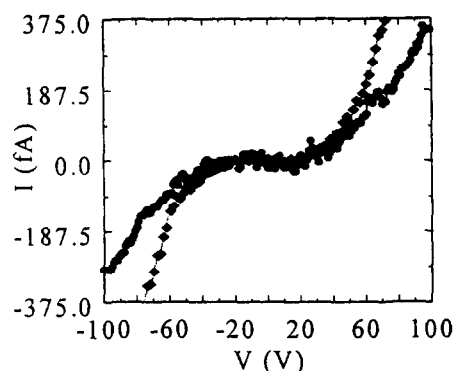
Figure 1. I vs V for the biopolymer-nanoparticle (●). Data from film [3] (◆).
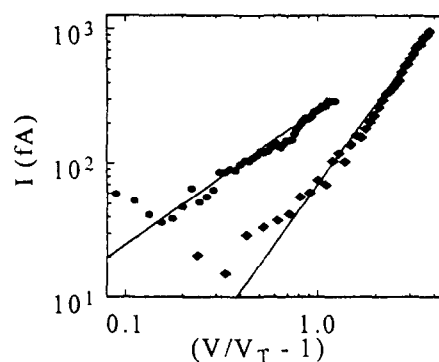

Figure 2. I as a function of the reduced voltage for the data shown in Figure 1.

expect $N \sim 200$ for this full disorder case. It is possible that less disorder is present in which case $\alpha(C/C_g)$ will be smaller and N larger. For example, N will be about 10^3 for an offset charge distribution spanning the range $\pm e/100$ [9]. Therefore, the minimum number of biopolymer units participating in the one-dimensional transport is approximately 30. Even if these were placed end to end the number is too small to bridge the electrodes. We conclude that the biomolecules form a complex network that has two-dimensional nets coupled together by individual biopolymer units. It is these single units that dominate the transport.

Well above threshold, the current through a one-dimensional array is predicted to approach $I \approx \alpha(C/C_g)e/RC_g(V/V_T -1)$, where R is the tunnel resistance. Assuming the sample is a single chain, $R \sim 5\times10^{11}$ Ω. Using the extended Hückel approximation to estimate the transmission through a straight alkanethiolate molecule [10], this value of resistance is expected for a chain about 2 nm long. This is close to a core spacing of $2(r\text{-}R) = 2.8$ nm, which is twice the ligand shell thickness.

4. SUMMARY

The room temperature I-V characteristics of ligand-stabilized metal nanoparticle attached to a biopolymer shows one-dimensional Coulomb-blockade behavior. The results are consistent with a metal nanoparticle network in which the transport is dominated by one-dimensional paths that contain a total of at least 200 nanoparticles.

REFERENCES

1. R. P. Andres, et al, Science 273, 1690 (1996).
2. T. Sato, H. Ahmed, D. Brown and B.F.G. Johnson, J. Appl. Phys 82 696 (1997).
3. L. Clarke et al. J. Vac. Sci. Technol. B 15, 2925 (1997).
4. L. O. Brown, J. E. Hutchison, J. Am. Chem. Soc. 119, 12384 (1997).
5. P. Delsing, T Claeson, K.K. Likharev and L.S. Kuzmin, Phys. Rev. B 42, 7439 (1990).
6. A.A. Middleton and N.S. Wingreen, Phys. Rev. Lett. 71, 3198 (1993).
7. G.Y. Hu and R.F. O'Connell, Phys. Rev. B 49, 16773 (1994).
8. J.A. Melson U. Hanke, H.-O. Müller and K.-A. Chao, Phys. Rev. B 55, 10638 (1997).
9. M. Stopa. Private communication.
10. M. Salmeron et al, Langmuir 9, 3600 (1993).