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The use of biopolymer templates to fabricate low-dimensional gold particle structures

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We report the current–voltage characteristics of gold nanoparticle–biopolymer networks at room temperature. The characteristics have features that are indicative of single-electron charging in ordered, one-dimensional chains of nanoparticles. From capacitance estimates and numerical simulations, we argue that the observed electrical behavior is related to the low size dispersion of the nanoparticles and the uniformity of the biopolymer lengths imbedded within the network.

Key words: nanoparticles, Coulomb blockade, biopolymer.

1. Introduction

Ligand-stabilized metal nanoparticles possess many qualities that facilitate the investigation of single-electron charging effects [1–5]. Because of their small size, typically $<$100 atoms, the Coulomb charging energy of the nanoparticles is at least an order of magnitude greater than the thermal energy ($k_{\mathrm{B}}T$) at room temperature [6]. Nanoparticles of this size can support single-electron charging effects at 300 K when the ligand shell forms a tunnel barrier of resistance greater than the resistance quantum [7, 8]. In addition to providing electrical isolation, the ligand shell can be chemically modified to facilitate coupling between nanoparticles or attachment to other molecules [9].

We report transport measurements on gold nanoparticles with ligand shells attached to a rigid biopolymer network through the interaction between the ligand shell and the biopolymer. The room-temperature electrical conductance of all such samples shows a distinct Coulomb gap at low-bias voltages. Many samples showed periodic structure at voltages above threshold. Periodic conductance features are well known to be associated with single-electron effects [10–15]. What is unusual about the data reported here is the fact that the voltage scale of the periodicity is several orders of magnitude greater than that found in other quantum dot or mesoscopic samples.

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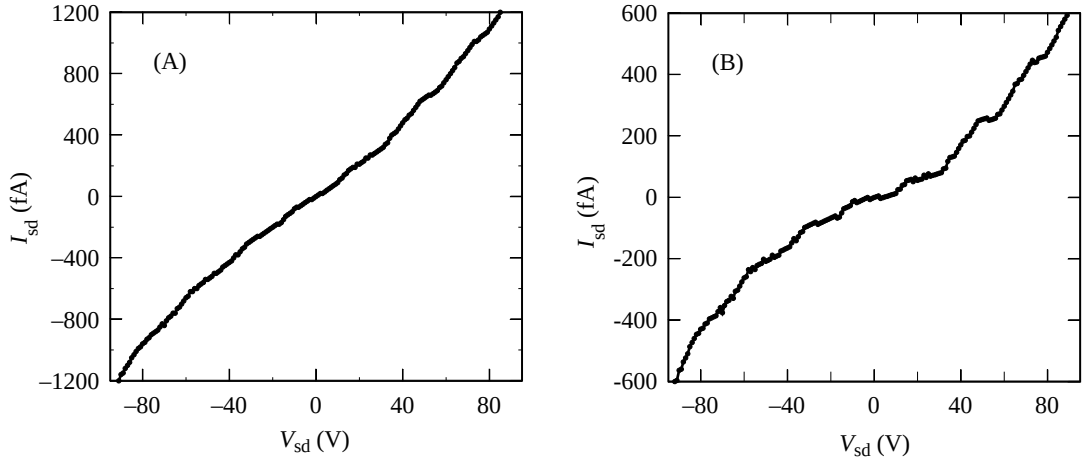

Fig. 1. A, The I–V characteristic of a poly-L-lysine-nanoparticle sample. B, The I–V data after subtraction of the background conductance of the undecorated biopolymer.

2. Experiment

Poly-L-lysine (54 000 amu) was deposited onto interdigitated gold electrodes with 15 μm spacings to form a framework to which gold nanoparticles were attached. The average length of the poly-L-lysine was 30 nm. The details of the fabrication have been reported elsewhere [16]. TEM measurements showed that the radius of the metal core was 0.7 nm, with a variation of $\pm 20\%$. The radius of the core and ligand shell together is estimated to be 2.1 nm.

Current–voltage (I–V) measurements were made in an electrically shielded vacuum chamber at room temperature [3]. Radio frequency (RF) electric fields could be applied by means of a dipole antenna placed close to the sample.

3. Results and discussion

Representative I–V behavior of the biopolymer–nanoparticle samples is shown in Fig. 1A. All samples exhibited nonlinear behavior, with many showing structure equally spaced in voltage. Control experiments showed little or no difference between the I–V characteristics of the undecorated biopolymer and the bare electrodes. When the data are corrected for the conductance of the undecorated poly-L-lysine, a blockade region and plateaus regularly spaced in voltage are clearly visible, as shown in Fig. 1B. For this sample the threshold voltage was $V_T = 12 \pm 1$ V, and the period of the oscillations was $\Delta V = 25 \pm 3$ V. In general, the ratio $\Delta V / V_T$ was frequently close to 2. Applying RF signals to the sample had no observable effect on the plateau structure.

Above threshold, the scaling $I \propto (V/V_T - 1)^\gamma$ was found to describe all sets of data, with $\gamma = 1.2 \pm 0.2$, as illustrated in Fig. 2. Here the error includes the uncertainty in the current measurement and the spread between different samples. Unlike the quadratic dependence found in thin films containing gold nanoparticles [3, 7, 8], this result is consistent with single-electron transport in both ordered and disordered one-dimensional systems where it is predicted that $\gamma \sim 1$ [17, 18]. Experiments on one-dimensional chains of tunnel junctions found $\gamma = 1.36 \pm 0.1$ [19]. Thus, from the current–voltage scaling above threshold, we conclude that regions of one-dimensional morphology dominate the transport in the biopolymer–nanoparticle network.

From the sample layout, the distance between the nanoparticle cores and the ground plane is expected

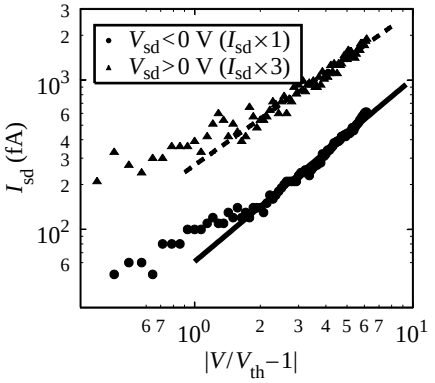

Fig. 2. Current versus scaled voltage. The solid circles (triangles) represent negative (positive) bias voltages. For clarity, the current values for positive bias have been multiplied by 3. The solid and dash lined are least square fits to the data and have slopes of 1.2 and 1.0, respectively.

to be relatively large. Thus the capacitance to ground, C_g, can be approximated by the self capacitance of a conducting sphere embedded in a dielectric shell. Assuming the ligand has a dielectric constant of 3, we estimate that $C_g \approx 0.14$ aF. Treating the adjacent nanoparticles as identical metal spheres of radius 0.7 nm whose centers are separated by a distance 4.2 nm, we estimate the maximum inter-particle capacitance to be $C_{dd} = 0.023$ aF. Using the above capacitance estimates in a conventional Coulomb blockade model [18] we obtain $V_T = 0.5$ V, which is at least an order of magnitude smaller than the threshold voltages measured.

Monte Carlo simulations [20] of the conductance characteristics of chains consisting of one, two and five nanoparticles with $C_g = 0.14$ aF and $C_{dd} = 0.023$ aF are shown in Fig. 3A. In the regime where $C_g \gg C_{dd}$, plateaus occur with a periodicity of about e/C_g. Also, these simulations show that the ratio $\Delta V/V_T$ is equal to 2 when there is little or no disorder and that the number of plateaus in the I–V characteristics is approximately equal to the number of nanoparticles in the chain. The effect of a variation in the values of C_g and C_{dd} is shown in Fig. 3B. The capacitance disorder due to the uncertainty in the measured nanoparticle radius (±20%) is not found to affect the periodicity of the plateaus. However, introducing an uncertainty of ±50% in C_g (±67% in radius) can destroy the periodicity. Variation of C_{dd} by ±50% had little or no effect on the I–V characteristics.

The simulations demonstrate that chains of nanoparticles where $C_g \gg C_{dd}$ will have I–V characteristics with properties similar to the data. However, the voltage scale needs to be addressed. Although conventional Coulomb staircase phenomena have been reported at 287 K in long chains of particles [12], to reproduce the structure seen in our data from a simple chain of clusters would require the nanoparticles to be unphysically small. For this reason, the origin of the structure is unlikely to come from a few smaller nanoparticles dispersed in the chain.

The voltage scale discrepancy may be explained if the biopolymer–nanoparticle network contains sections that are not in Coulomb blockade. These sections could form a bias network for those in blockade, thus reducing the voltage across each section in blockade. The weakly conducting sections could result from regions in which the capacitance of the nanoparticles is increased. Also, the background conductance between the electrodes themselves could provide a bias network. The size of the electrodes causes a high degree of spatial averaging over the network. Therefore, if the idea of a resistive bias network is correct it suggests that the conductance oscillations are insensitive to the local arrangement of the poly-L-lysine network. This implies that their origin must be related to system parameters that have a high degree of uniformity, such as the molecular weight (length) of the poly-L-lysine, or the size (capacitance) of the nanoparticles.

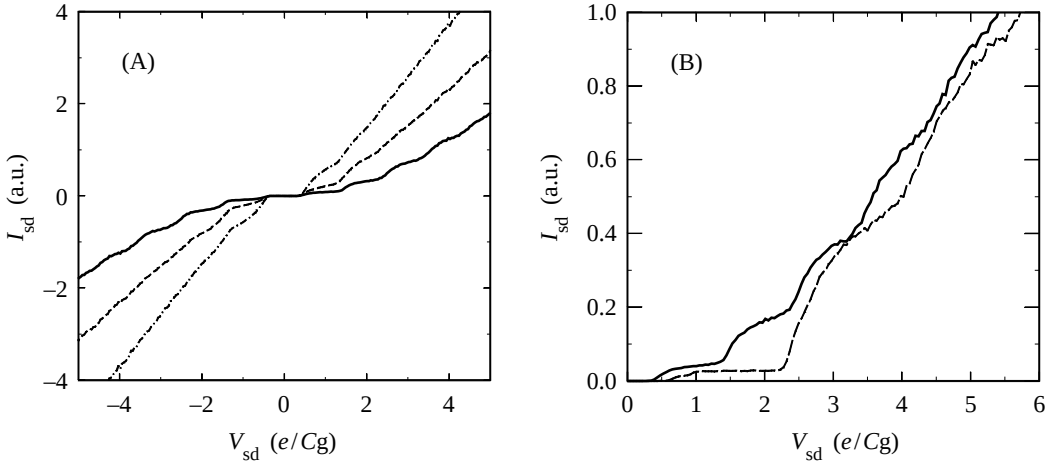

Fig. 3. A, Monte Carlo simulations of chains of one (— • —), two (— —) and five (——) nanoclusters in series. B, Monte Carlo simulations of five nanoclusters in series with ±20% (——) and ±67% (— —) variation in nanocluster radius. All simulations were done for a temperature $T = 300$ K.

4. Summary

In summary, we have measured the room-temperature transport in a biopolymer–nanoparticle system. The almost linear relationship between current and voltage above threshold suggests that the poly-L-lysine molecules act as a one-dimensional template for the gold nanoparticles. From the observed plateau structure and capacitance estimates, we believe the one-dimensional sections of the network contain at least five nanoparticles. Single-electron charging effects are expected to be sensitive to the size distribution of nanoparticles and to the length of the poly-L-lysine biopolymer, which may be the reason we do not observe the plateau structure in all samples.

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