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Determination of Single Molecule Conductances of Alkanedithiols by Conducting-Atomic Force Microscopy with Large Gold Nanoparticles

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Measurement of the electronic properties of single molecules is an essential step in developing an understanding of molecular electronics.[1] Highly reproducible data were first obtained with a self-assembled molecular junction that consisted of a dithiolated molecule, inserted into a matrix of alkanethiols, attached at one end to a gold substrate via a thiol−gold linkage and at the other end to a gold nanoparticle also via a thiol−gold linkage. The electrical circuit was completed by pushing a conducting-atomic force microscope (c-AFM) probe into the gold nanoparticle (Figure 1a).[2] Small, but significant disagreements with the results of first principles calculations[3] were tentatively attributed to the electronic properties of the gold particle.[4] Better agreement was produced with the scanning tunneling microscopy (STM) repeated break-junction (BJ) method,[5,6] a technique that has now yielded data that is broadly in agreement with theory for a number of molecules.[7,8] The self-assembled molecular junction method has certain advantages. Current−voltage ($I-V$) curves may be continuously recorded, and the environment of the molecule is somewhat better defined. The goal of this current work is to demonstrate that the original anomalies were indeed a consequence of the use of a small gold particle, and that the use of a larger particle yields data that are now broadly in agreement with the BJ method.

Our original study utilized small gold particles (1.5 nm in diameter) on the basis of the assumption that a metallic junction would be formed with the gold coated AFM probe.[2] Careful analysis of the data[4] indicated that this assumption was invalid. The contact resistance between the AFM probe and the gold nanoparticle was clearly large enough to allow the nanoparticle to charge independently, distorting the $I-V$ curves both through Coulomb blockade[9] and the intrinsic electronic gap in the small particle.[10] The combination of both these effects prevented us from carrying out a full theoretical analysis of the data from these experiments.[4]

For the present study, we have synthesized larger gold particles (5.4 nm diameter). These are large enough to eliminate the problem of an intrinsic electronic gap at room temperature[10] and present a small Coulomb blockade barrier. We measured the single molecule conductance of three different alkanedithiols using the larger particles, obtaining data for the decrease of conductance with chain lengths that are in agreement with the BJ method. Interestingly, the absolute conductance is still slightly smaller than measured with the BJ method, an effect we tentatively attribute to compression of the molecule in the self-assembled molecular junction (compared to the tension in a BJ experiment).

Large gold nanoparticles protected by tetraoctylammonium bromide were prepared by the two-phase method reported in the literature.[11] The size of the nanoparticles was determined by transmission electron microscopy to be 5.4 ± 1.0 nm. A gold-coated mica substrate, annealed in a hydrogen flame, was first immersed into a monothiol solution to form a self-assembled monolayer, and then immersed into a dithiol solution to insert the dithiol molecules into the defects in the monothiol matrix, and finally treated with the nanoparticle solution to chemically attach the nanoparticles to the remaining end of the dithiol. Three different samples were prepared from octanethiol/octanedithiol, decanethiol/decanedithiol, and dodecanethiol/dodecanedithiol. They are labeled as the C8, C10, and C12 samples, respectively.

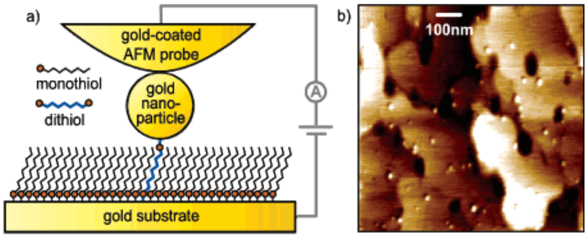

Figure 1. (a) Schematic illustration of the metal−molecule−metal junction to determine the single molecule conductance of the target dithiol molecule by c-AFM with a gold nanoparticle and (b) typical AFM image of the C8 sample taken in toluene with a set force of 7 nN.

The c-AFM measurements were carried out using a gold-coated silicon cantilever operating in toluene flushed with Ar at room temperature. The set-point force was 7−14 nN. Figure 1b shows a typical AFM image of the C8 sample. The gold nanoparticles are clearly seen on the surface and they are well-isolated from each other. Their apparent size in the image is 10−25 nm (larger than the actual size because of the ca. 10 nm radius of the AFM probe). As a control experiment, a pure monothiol monolayer without dithiol was similarly treated with the nanoparticle solution, but nanoparticles were not observed by AFM, showing that the nanoparticles on the mixed monolayer are chemically bonded to the outer end of the dithiol molecules.

After imaging, the AFM probe was placed on the nanoparticle and $I-V$ curves were collected by applying bias between the substrate and tip. Representative $I-V$ curves of the C8 sample are shown in Figure 2a. In contrast to the small nanoparticle case,[2] where the $I-V$ curves had a region of suppressed current around zero bias, the $I-V$ curves in this system are quite linear. Theoretical calculations of $I-V$ curves[4,9] were performed taking the charging effect into account (see Supporting Information), and they showed that the $I-V$ curve is almost linear for a 5.4 nm nanoparticle in contrast to the significant Coulomb blockade in a 1.5 nm nanoparticle. A "particle-in-a-box" estimate of the level spacing[10] for a 5.4 nm particle yields a gap of 1.5 meV, in rough agreement with experiment and completely negligible at room temperature. Therefore, the linear $I-V$ curves are expected for the 5.4 nm particle. When the probe was placed on the matrix, or when the measurement was performed on pure monothiol monolayers without nanoparticles, the currents were a factor of 10^2-10^3 smaller. This shows that the current response is from the dithiol spanning the junction.

Linear fits to each $I-V$ curve yielded the apparent conductance, and the histogram of the apparent conductances was constructed

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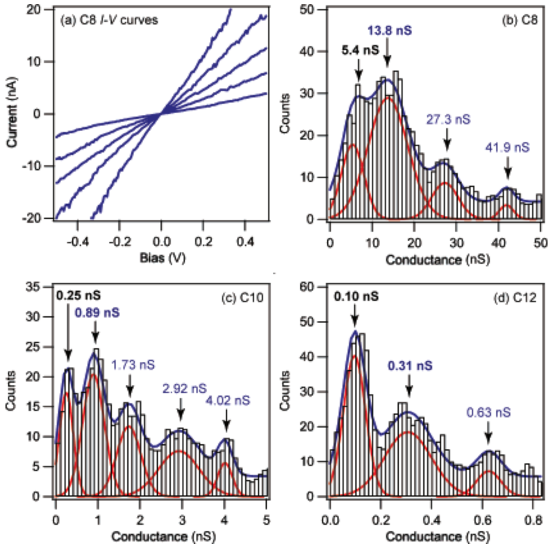

Figure 2. (a) Representative $I-V$ curves of the C8 sample and the apparent conductance histograms of the C8 (b), C10 (c), and C12 (d) samples, respectively.

from over 1000 $I-V$ curves for each molecule. Figure 2 panels b, c, and d show the results for the C8, C10, and C12 samples. It is apparent that these data are much more broadly distributed than those originally reported by Cui et al.[2] The histograms were analyzed by fitting Gaussian functions to determine the location of the conductance peaks. In each histogram, the peak conductances to the right of the second peak are very close to being integral multiples of the conductance of the second peak which was taken to represent the single molecule conductance (the higher multiples corresponding to integer numbers of molecules spanning the junction). Multiples of the first peak are difficult to see because they overlap with the larger conductance peaks arising from the dominant feature. The BJ studies also showed two sets of single molecule conductances, probably due to differences in the sulfur−gold contact configuration (on-hollow and on-top adsorption of the sulfur atom on the gold (111) lattice).[12,13] We label these two features as HC (high conductance) and LC (low conductance), respectively.

More than three separate experiments on each molecule were done to get the average values. HC and LC were determined by correcting for Coulomb blockade (Supporting Information) and the results are shown in Figure 3a (along with those obtained by the BJ method for comparison[12]). The HC values roughly agree with those determined by the BJ method but are still lower by 15−20%. It has been reported that conformation of an alkane chain significantly effects the electron transmission and gauche defects in the chain lower the conductance.[14,15] A significant number of gauche defects are to be expected near the top of these monolayers,[16] an effect we expect to be significantly enhanced owing to the compression of the film by AFM. The deformation of the monolayer was calculated to be 0.45 nm for 7 nN using the Hertzian model.[17] Moreover, the dithiols should be predominantly inserted into defect sites of the matrix, in which poorer packing allows conformational fluctuations. We expect that the chain takes on a fully extended trans conformation in the BJ system. Therefore, the slight discrepancy between the results of the two methods might be explained by the conformational differences. However, this speculation does not hold for the LC values, in which the values obtained in this study are larger, a point that needs clarification in future work.

a)

sample	method	HC (nS)	LC (nS)
C8	**c-AFM**	**16.1 ± 1.0**	**5.6 ± 2.3**
	BJ	19.4	4.0
C10	**c-AFM**	**1.37 ± 0.35**	**0.40 ± 0.11**
	BJ	1.6	0.28
C12	**c-AFM**	**0.35 ± 0.04**	**0.08 ± 0.02**
	BJ	no data	no data

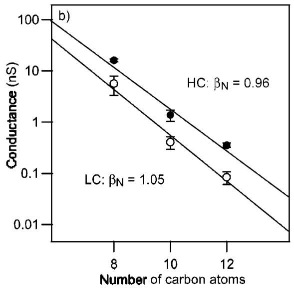

Figure 3. (a) Single molecule conductances of the three alkanedithiols determined in this work and by the BJ method for comparison and (b) semilog plots of the HC (closed circles) and LC (open circles) versus the number of the carbon atoms. The error bars show the standard deviations.

In conclusion, we have demonstrated that a large gold nanoparticle can eliminate the problems of charging and quantized levels and that the c-AFM measurements using large nanoparticles give reasonable values for single molecule conductances and their distance-dependence. This provides a valuable addition to the existing BJ method.

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Supporting Information Available: Complete details of the experiments and the supporting text and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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