Measurement of Electron Transport Properties of Single Molecules

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The conductance of a single molecule covalently connected to two gold electrodes can be determined by the statistical analysis of many repeatedly created gold-molecule-gold junctions. Conductance histograms reveal well-defined peaks at integer multiples of a fundamental conductance, which is used to identify the average conductance of a single molecule. The large width of the peaks indicates considerable variations in conductance of individual molecular junctions due to difference in the microscopic details of molecule-electrode contacts. Using the method, electron transport properties of a variety of molecules, from \(N\)-alkanedithiol molecules to DNA duplexes, have been studied. [DOI: 10.1143/JJAP.44.5344]

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1. Introduction

The ability to measure electron transport through single molecules is a basic requirement in molecular electronics.\(^1\) It also allows one to study charge transport, a phenomenon that plays vital roles in many chemical and biological processes, on a single-molecule basis. While recent advances are impressive,\(^2\)–\(^10\) it is still a nontrivial task to directly measure the conductivity of a single molecule electrically wired to two electrodes. Large disparities in molecular conductivity have been found between different experiments even for simple \(N\)-alkane molecules. The reported characteristics of DNA conductivity vary from insulator and semiconductor to metal and superconductor, which further illustrates the difficulty of the task.\(^11\)–\(^15\)

To reliably measure the conductance of a molecule, one must provide a reproducible electronic coupling between the molecule and probing electrodes.\(^16\)–\(^19\) Due to the difficulty in forming microscopically identical molecule-electrode contacts, a statistical analysis of a large number of molecular junctions is necessary in order to obtain a complete picture. One must also find a signature for identifying that the measured conductance is due to not only the sample molecules but also a single sample molecule. Furthermore, for biologically relevant molecules such as DNA, it is highly desirable to carry out the measurement in aqueous solutions in order to preserve the native conformation of the molecule.

For molecules with a metal redox center, single-electron charging effect has been used as a signature.\(^20\)\(^–\)\(^25\) For many other molecules, a different signature is required. Cui et al.\(^16\) reported a method of using a conducting atomic force microscope (AFM) to measure the resistance of octanedi-thiol that has one end anchored to a gold substrate and the other end attached to a gold nanoparticle. The work represents the first measurement of a molecular junction with statistical analysis. However, the procedure involves several elaborate assembly steps, and the measured resistance is complicated by the Coulomb blockade effect due to finite contact resistance between the AFM probe and gold nanoparticle, which needs to be corrected.\(^20\)\(^,\)\(^21\) We have developed a relatively simple method of measuring single-molecule conductance by repeatedly forming thousands of molecular junctions in which molecules are directly covalently connected to two gold electrodes.\(^22\)\(^–\)\(^26\) The method also allows the exposure of molecules to aqueous solution, which is particularly suitable for studying biologically relevant molecules.

2. Method

The method is illustrated schematically in Fig. 1. We repeatedly form thousands of individual molecular junctions by moving a gold scanning tunneling microscope (STM) tip into and out of contact with a gold substrate in the presence of sample molecules. Because each molecule we study is terminated by two appropriate linkers (e.g., bipyridine and dithiol groups) that can strongly bind to metal electrodes, it can bridge the STM tip and gold substrate and form a molecular junction. During the process, current between the tip and substrate electrodes is recorded at a fixed bias voltage.

During the initial step of pulling the tip out of contact with the substrate, conductance decreases in a stepwise manner, with each step occurring preferentially at an integer multiple of conductance quantum \(G_o = 2e^2/h\), which is due to the formation of an atomic scale gold contact between the tip and the substrate. After the gold contact is broken, a new series of steps at lower conductance appear. We attribute the conductance steps observed after the breakdown of the gold contact to the formation of molecular junctions. The lowest step corresponds to a single molecule between the two gold electrodes.

This conclusion is supported by the following observations. First, in the absence of molecules, no conductance step significantly lower than \(1G_o\) is observed. Second, the conductance peaks are located at different conductances...
for different molecules. For instance, the conductance (peak position) of alkanedithiol decreases exponentially with molecule length.\textsuperscript{22)} Third, we have measured conductance and force applied to the molecule simultaneously, which directly confirms that the conductance steps are due to the breakdown of individual molecules.\textsuperscript{24)} We note that the conductance steps do not always occur at the same conductance, reflecting variations in the microscopic details of molecule-electrode contacts. A statistical analysis of a large number of measurements is thus necessary. The corresponding histogram shows pronounced peaks located at integer multiples of fundamental conductance, which is identified as the average conductance of a single molecule.

The current–voltage ($I$–$V$) characteristics of single molecular junctions can be obtained by two different ways. The first one is to perform statistical analysis at different bias voltages. The peak positions in conductance histograms at different bias voltages are used to construct $I$–$V$ curves. The $I$–$V$ curves obtained by this method are the average of thousands of molecular junctions, but it may wash out interesting features due to individual molecular junctions. The second method has been developed to overcome this problem. In this method, we manually control the pulling process by applying a voltage to the piezoelectric transducer (PZT) of the STM tip. During the pulling process, we monitor conductance continuously until it decreases to the lowest conductance step, corresponding to the formation of a single molecular junction. We then hold the STM tip position and measure current while sweeping bias voltage. This method requires a constant distance between the STM tip and the substrate. With our homemade setup, we can stably hold the tip position for many seconds to several minutes, which is sufficiently long to record $I$–$V$ curves.

3. Results

3.1 4,4’-bipyridine

4,4’-bipyridine is a good model molecule for testing the experimental method because 1) it is terminated with two pyridine groups that can bind strongly to gold electrodes, and 2) it is fairly conducting due to its conjugate structure. We performed the measurement by driving a gold STM tip in and out of the contact with the gold substrate in 1 mM 4,4’-bipyridine aqueous solution (with 0.1 M NaClO$_4$ as the supporting electrolyte for potential control). During the pulling process, conductance decreases in a stepwise manner with each step occurring preferentially at an integer multiple of conductance quantum, $G_0 = 2e^2/h$. A histogram constructed from one thousand such conductance curves shows pronounced peaks at $1G_0$, $2G_0$ and $3G_0$. This is conductance quantization, which occurs when the size of a metallic contact decreases to a chain of gold atoms.\textsuperscript{27,28)} With the last gold atom broken, a new series of steps at a lower conductance appear in the presence of 4,4’-bipyridine [Fig. 2(a)]. The corresponding histogram shows pronounced peaks near 0.01 $G_0$, 0.02 $G_0$ and 0.03 $G_0$ [Fig. 2(b)], two orders of magnitude lower than those arising from conductance quantization. We ascribe this set of conductance steps to the formation of stable molecular junctions, and the conductance peaks at $1 \times$, $2 \times$, $3 \times 0.01 G_0$ to one, two, and three molecules in the junctions, respectively. We performed the following control experiments.

First, in the absence of molecules, no peaks below $1 G_0$ are observed in the conductance histogram. Second, in order to test that the conductance peaks are due to the formation of stable molecular junctions, we performed the measurement in the presence of 2,2’-bipyridine. The molecule is structurally similar to 4,4’-bipyridine except for the positions of the two nitrogen atoms, which prevent the molecule from simultaneously binding to two electrodes.\textsuperscript{29)} As expected, we did not observe the conductance peaks in the presence of 2,2’-bipyridine. Third, since the binding strength of 4,4’-bipyridine to a gold electrode depends on electrode potential,\textsuperscript{30,31)} we performed the experiment at different potentials (with respect to a reference electrode in the solution). At negative potentials that the molecule does not bind to the electrodes, the conductance peaks disappear. The peaks reappear at positive potentials.

It is interesting to note that the average distance over which the molecular junction stretched before breakdown can be as large as several angstroms. Clearly, it is impossible to stretch the molecule over such a large distance. The reason is that most stretching occurs at Au-Au contacts,
rather than in the molecule itself. This is supported by the observation that the molecule is much stiffer than the Au-Au bonds at the contacts, and by the elastic constant measurement\(^2\)\(^4\) that shows that the effective elastic constants of molecular junctions are similar to that of pure Au-Au contact.

### 3.2 Peptide molecules

Peptide molecules are interesting because their lengths and sequences can be easily and systematically controlled. Peptides are also the building blocks of proteins, and they possess various molecular recognition capabilities. For example, a simple three-amino-acid peptide, cysteamine-glycine-cysteamine (Cysteamine-Gly-Cys), can recognize and bind to Cu\(^{2+}\) and Ni\(^{2+}\) ions. We have studied several short peptides (3–5 amino acids long), each is terminated by two thiol groups that provide electrical contacts to gold electrodes.\(^2\)\(^6\) Figure 3 shows the conductance measurements for Cysteamine-Gly-Cys. The conductance histogram shows peaks similar to those of 4,4\(^0\)-bipyridine [Fig. 3(a)]. The first peak in the conductance histogram of Cysteamine-Gly-Cys is at \(G_0 = 10^{-2} \text{e}^2/\text{nm}\), which is much less conductive than 4,4\(^0\)-bipyridine. The observed higher conductivity of 4,4\(^0\)-bipyridine is at least partially due to its conjugate structure.

Since peptides are not as rigid as 4,4\(^0\) bipyridine, there is a possibility that the two thiol terminals of a peptide molecule bind to a single electrode. This configuration, however, should not contribute to the conductance histogram significantly because it will not stretch the Au-Au contact and thus produce no steps or very short steps in the transient conductance curves. Besides, the undefined contact at one end will lead to an undefined conductance, which will not lead to pronounced peaks in conductance histograms. Finally, we performed measurements on molecules with only one side that can bind to electrodes, and found no pronounced peaks in the conductance histograms.

The conductance of peptides decays exponentially with the length of the molecule, indicating that similar to alkanedithiols, electron tunneling through peptide chains is the predominant conduction mechanism. The decay constant \(\beta\) for peptides is \(\sim 0.87 \text{ Å}^{-1}\), which is similar to that of alkanedithiol [Fig. 3(c)]\(^2\)\(^2\). Unlike the symmetric \(I-V\) curves for alkanedithiols and 4,4\(^0\)-bipyridine, the \(I-V\) characteristic curves for peptides are, however, asymmetric, which is expected because of the asymmetric structure of peptides [Fig. 3(b)]. Another interesting difference between peptides and alkanedithiols is that the conductance of peptides is, in general, sensitive to the pH of the solution [Fig. 3(d)]. This sensitive dependence is attributed to the protonation/deprotonation of charge groups, such as the amine and carboxyl groups. Finally, as we have already mentioned, many peptides bind to metal ions strongly. We have observed that upon metal ion binding conductance increases significantly, which is due to metal ion binding inducing conformational change in the peptide.\(^2\)\(^6\) The metal ion itself may also introduce new electronic states near the Fermi energy level of the electrodes and mediate a more efficient electron transport through the peptides.

### 4. Conclusions

We described above a method of measuring the conductance of single molecules. The method offers the
following features: 1) It can rapidly produce a large number of measurements on different molecular junctions, which provide a complete picture on the variations in the microscopic details of individual molecular junctions by statistical analysis. 2) The peaks in the conductance histograms are found to locate at integer multiples of fundamental conductance, which is used to identify single-molecule conductance. 3) Since each molecular junction is formed by pulling two electrodes apart, only molecules attached to two electrodes contribute to the measured conductance. 4) The molecules are exposed to solutions, which is particularly suitable for studying biologically relevant molecules. However, the method is clearly not compatible with conventional solid state electronic devices. In addition, the statistical approach allows us to determine the average conductance of a single molecule, but it does not solve the problem of large variations in the microscopic details of individual molecular junctions.

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