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High probability of single molecule junction formation with Ag electrodes

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ABSTRACT

We use a scanning tunneling microscope-based break-junction technique to compare the probability of the formation of a single-molecule junction for a series of amine-terminated oligophenyl and alkane species using either Ag or Au as electrodes. For all molecules, we find that there is a significantly higher probability of junction formation when using Ag electrodes than with Au electrodes. We also find that longer molecules have a higher probability than shorter molecules to form a junction for both Ag and Au electrodes. For all molecules, the measured molecular junction length that is formed with the Ag electrodes was longer than that formed with Au electrodes. Furthermore, we can make a single atomic oxygen junction and can measure its conductance using Ag electrodes. These observations are attributed to a narrower gap of the Ag electrodes compared to that of the Au electrodes after the metal contact ruptures. Since there is a high probability of a molecular junction forming when using Ag electrodes, we can therefore perform a statistical analysis within the context of the material properties that are suitable for future molecular electronics.

1. Introduction

A statistical analysis of the electronic transport experimentally measured in single-molecule junctions is of critical importance for the design of molecular electronic circuits since the electrical properties of the metal–molecule junctions are extremely sensitive to the binding geometry, and there is uncertainty in terms of the structures at the junctions [1–6]. The scanning tunneling microscope (STM) and mechanical break junction (MCBJ) techniques have been used to investigate the electrical properties of single-molecule junctions [7–12]. However, these techniques are very costly, and it takes a long time to build the experimental setup with high-vacuum and low temperature. Therefore, it is not easy to analyze statistically such single molecule junctions using these techniques. The conducting atomic force microscope (AFM) can also be used to investigate the electrical properties of a thiol-terminated molecule that has one end of the molecule bonded to a gold substrate and the other end attached to a gold nanoparticle [13]. In this work, the properties of a molecular junction were measured hundreds of times so that a statistical analysis could be performed. However, this method involves several delicate assembly processes, and analysis of the measured conductance is complicated by the effects of the Coulomb blockade that results from the finite contact resistance between the Au-coated AFM probe and the gold nanoparticle [14]. Furthermore, the AFM is not available to make the single molecular junctions using the Au-coated probe. Therefore, we need to find the new technique to measure properly the conductance of the single molecule. The scanning tunneling microscope-based break-junction (STM-BJ) technique is one of the most versatile techniques, and it can be used to create single metal-molecule junctions under ambient conditions [15–19]. The STM-BJ is versatile, inexpensive, very fast, and easy to load and measure the sample compared to the original STM setup. It exhibits reliable and reproducible conductance values when proper linkers-such as amine or thiols-are used to attach the molecules to the junction contacts. Due to this reduced variability, we can determine the electrical properties in a statistically meaningful manner for specific single-molecule junctions. This measurement, however, has less than 30% probability of forming a junction for small molecules as a low possibility of junction formation due to the large gap size between the two Au electrodes [3,16,20]. The previous results show that the single molecular junction can be formed with Ag electrodes for measuring the conductance and the electrical properties [21–24].

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In this study, we have carried out measurements of the probability of junction formation for a series of amine-terminated oligophenyl and alkane species when using Ag or Au electrodes under a STM-BJ technique. For all molecules, we obtain a significantly higher probability of junction formation for Ag electrodes than for Au electrodes, and we can see that longer molecules have a higher probability of forming a junction compared to shorter molecules for both Ag and Au electrodes. The molecular elongation measured when junctions were formed with Ag electrodes is longer than that with Au electrodes. Furthermore, we are able to measure the conductance of a single oxygen atom formed with Ag electrodes (Ag–O–Ag) with a probability of ~25% for junction formation, which is comparable to that of the formation of an Au-benzene-Au junction. These observations are attributed to a narrower gap between the Ag electrodes than between the Au electrodes after the metal contact ruptures.

2. Experimental procedure

We measure the probability of the formation of a junction by repeatedly forming and breaking Ag and Au point contacts in the presence of target molecules by using a modified STM-BJ setup that was previously described in detail [15–17]. A mechanically polished Ag slug (Alfa-Aesar 99.99% purity) with a freshly cut Ag wire tip (Alfa-Aesar, 99.9985% purity) was used for the Ag measurements. We also deposit a 100-nm Au film on the mica substrate and use the Au/mica substrate with an Au wire (Alfa-Aesar, 99.998% purity) to make the Au measurements [15]. The STM operates in ambient conditions at room temperature, and the junctions are broken in a 1 mM solution of the molecules in 1,2,4-trichlorobenzene (Sigma–Aldrich 99% purity). Each conductance measurement starts by moving the tip of the STM into the substrate to create a metal point-contact with a conductance of at least 15 G_0. This ensures that a new electrode structure is created for each measurement. The tip is then withdrawn from the substrate at a speed of about 200 nm/s while the current is recorded at a fixed applied bias voltage of 50 mV at a 40 kHz data acquisition rate. This yields a conductance (current/voltage) versus displacement trace. For all measurements reported here, thousands of curves were collected to allow for detailed statistical analysis.

3. Results and discussions

Fig. 1a shows the schematic diagram of the molecular junctions that form during the metal-metal contact rupture for the Ag and Au electrodes. Initially the electrodes have a 1 G_0 ($G_0 = 2e^2/h$, the quantum conductance) metal-metal contact for both Ag and Au electrodes. These undergo an initial relaxation that opens up the gap distance (D) of the Ag and Au electrodes as soon as the contact is ruptured, within a 10 μs time resolution. This could be due to a relaxation of the electrodes, which were elastically stretched in the rupture process. Since the gap distance for Ag is smaller than that of Au [15], the molecule can be inserted in this small gap, and the metal-molecule-metal junction is formed more easily with Ag than with Au. The most of the molecules can bind onto the small gap of Ag electrodes, however a number of molecules could not bind onto the Au electrodes due to the large gap of the electrodes as marked by the "X" in Fig. 1a. This means that Ag electrodes can have a higher probability of forming a junction compared to that of Au electrodes Of course, the molecules can be inserted in the electrode gap before the formation of the gap and it can be more frequently happed for the long molecule than the short molecule. Furthermore, the thiol-terminated molecules can bind more easily than the amine-terminated molecules onto Ag or Au electrodes before metal atomic rupture due to the strong covalent bonding [25,26].

We measure the gap distance created after the Ag and Au metal contacts rupture, as shown in previous studies [15,27]. Briefly, we elongate a metal contact until it ruptures, and then we push the electrodes back together to determine the net distance that the electrodes need to move before a contact with a conductance of 1 G_0 is formed. The gap distance is the net distance measured for both the Ag and Au metal contacts without additional molecules. Fig. 1b

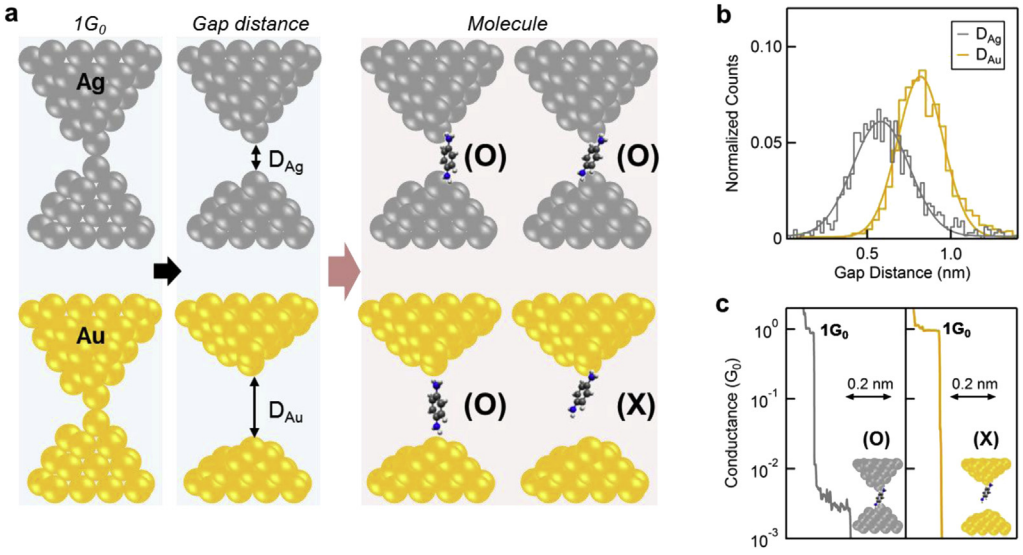

Fig. 1. (a) Schematic diagram of molecular junctions with Ag (i) and Au (ii) electrodes. After 1 G_0 metal-metal contacts are made for both Au and Ag, these undergo an initial relaxation that opens up the gap distance (D) as soon as the contact is ruptured. Finally the molecule can be inserted more easily into Ag electrodes when compared to those made of Au due to the smaller gap distance of Ag. The Ag has many possibilities of the molecular binding junction structures due to the small gap distant. However, the Au has only the fully elongated junction binding structure with large gap distance as marked by "O" resulting in the small probability of junction formation. (b) Normalized histogram of the gap distance for Ag (gray, D_{Ag}) and Au (yellow, D_{Au}) electrodes. (c) Sample conductance traces for 1,4-disminobenzene measured with Ag (gray) and Au (yellow) electrodes. The inset shows how Ag electrodes have a molecular junction formation but Au electrodes have no molecular junction formation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)