Measurement Environment Dependency of Single Molecule Conductance

Masateru Taniguchi,*[1,2] Kosuke Morimoto,[1] Makusu Tsutsui,[1] and Tomoji Kawai*[1]
[1]*The Institute of Scientific and Industrial Research, Osaka University,*
8-1 Mihogaoka, Ibaraki, Osaka 567-0047
[2]*PRESTO, Japan Science and Technology Agency, Honcho, Kawaguchi 332-0012*

(Received July 14, 2008; CL-080693; E-mail: taniguti@sanken.osaka-u.ac.jp)

In order to investigate the measurement environment dependency of single molecule conductance, the lifetime of Au single-atom contacts and the conductance of a metal complex were investigated in solution and vacuum using a nanofabricated, mechanically controllable break junction (nano-MCBJ). The lifetime of Au single-atom contacts in a solution is shorter than that in vacuum. Single molecule conductance of a metal complex was found to be independent of the measurement environment.

The ability to perform single molecule conductance measurement is one of the milestones necessary to realize a nanoscale molecular device, since conductance measurement of an electrode–molecule–electrode (EME) junction is indispensable to evaluate the device characteristics and physical properties of a single molecule device. Conductance measurements of EME junctions[1] have been performed both in vacuum and solution using a scanning probe microscope[2] and MCBJ.[3] In particular, single molecule measurement using MCBJ not only achieved a successful conductance measurement but also led to inelastic tunnel spectroscopy and electrochemical field-effect transistors, exploring new properties of EME junctions. However, most of the reported measurements are on single molecule conductance in either vacuum or solution, and how the measured conductance depends on the measurement environment has not been investigated. In particular, it is expected that single molecule conductance in solution differs from that of vacuum owing to changes in both potential and molecular structure.

Here we report how the measurement of single molecule conductance depends on the measurement environment. The stability of Au single-atom junctions in each environment was estimated by comparing the lifetime of the junctions in solution and vacuum; indeed, the stability of EME junctions has a big influence on single molecule conductance. Next, we evaluated the single molecule conductance of bis(1,3-dithiole-2-thione-4,5-dithiolato)nickel $[Ni(dmit)_2]^-$, which is known as a metal complex that gives rise to an organic conductor,[4] in both solution and vacuum.

A nano-MCBJ is devised using nanofabrication technologies.[5] The tetra-*n*-butylammonium bis(1,3-dithiole-2-thione-4,5-dithiolato)nickel(III) complex $(n\text{-}Bu_4N)[Ni(dmit)_2]$ was purchased from Tokyo Chemical Industry Co., Ltd. In an effort to study the stability of Au single-atom contacts and single molecule conductance in solution, we placed a Teflon ring on the junction and filled it with an organic solvent. To form single-atom contacts, we first break the nanojunction immersed in 1,2,4-trichlorobenzene (TCB) by bending the substrate into a three-point bending configuration. After this initial breaking process, we released the bending force gently by manipulating piezoactuator motion to re-create the Au nanocontacts. Subsequently, we stretched the junction in a controlled manner using our resistance feedback program.[5] Under vacuum conditions, initial rupture of MCBJs is exhibited in a TCB solution of $[Ni(dmit)_2]$ salt (1 μM) used to adhere the molecules to the freshly exposed metal surfaces. The junction displacement rate (ν_d) was set to 0.001 nm/s because a slow ν_d allows the junctions to break spontaneously via thermal fluctuations under negligible forces.[6] All measurements were carried out at room temperature.

Figure 1a shows the typical conductance change observed

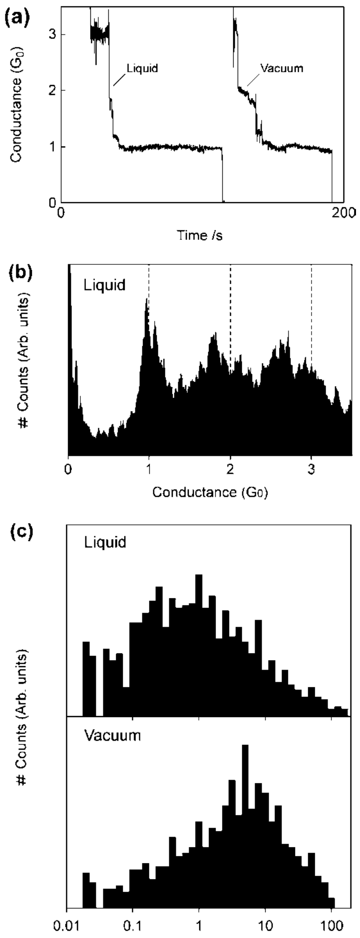

Figure 1. (a) Conductance curves measured during breaking, (b) conductance histogram in liquid environment (1,2,4-trichlorobenzene: TCB), and (c) lifetime (τ) distribution of Au single-atom contacts in solution and vacuum. The stretching rate was set to 0.001 nm/s.

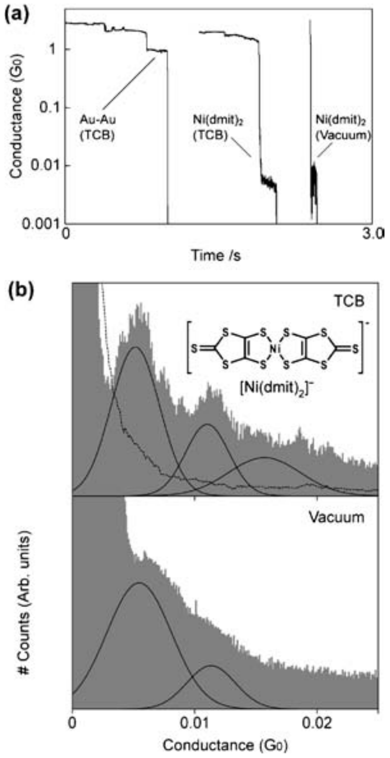

Figure 2. (a) Conductance curves measured during breaking and (b) conductance histograms of Au–[Ni(dmit)$_2$]$^-$–Au junctions. The curves are Gaussian fit to the peak profiles. The monotonous decay line shows the histogram of Au single-atom contacts.

during junction breaking in vacuum (right) and liquid (left) under a dc bias voltage of 0.1 V. The 1 G_0 (G_0 is the conductance quantum) plateau signifies the formation of a single-atom contact. The corresponding pronounced peaks appear at 1, 2, and 3 G_0 in the conductance histograms constructed from 1000 conductance curves (Figure 1b). There is no appreciable difference in conductance curves and histograms obtained in liquid as well as vacuum.

We next performed statistical analysis on junction stability by constructing conductance plateau length histograms. The length of 1 G_0 plateaus denotes the lifetime τ of single-atom contacts. τ is extracted from each of the 1000 conductance curves by obtaining the period of the junction conductance within a range of 0.8–1.2 G_0. As shown in Figure 1c, τ distributions are qualitatively the same in both liquid and vacuum environments; the distribution is broad for about four orders of magnitude, reflecting variation in the junction configurations, while the presence of a single-peak structure indicates preferential formation of a single-atom contact with a specific geometry. Although Figure 1c clearly shows that the average τ in a liquid environment is shorter than that in a vacuum and the origin of the shorter lifetime in a liquid environment than that in a vacuum is an open question, it is long enough to measure single molecule conductance.

We studied the single molecule conductance of [Ni(dmit)$_2$]$^-$ in a TCB solution. [Ni(dmit)$_2$]$^-$ molecules could be coordinated to the electrodes through sulfur atoms.[7] Figure 2a shows the typical conductance change observed during breaking in vacuum (right) and liquid (middle) under a dc bias voltage of 0.2 V. The conductance plateau corresponding to a single gold atom contact was observed at 1 G_0, and a conductance plateau was observed with sufficient frequency at lower than 0.01 G_0 in a solution of the metal complex. No conductance peaks were observed below 1 G_0 in a pure organic solvent (the monotonous decay line in Figure 2b. The quantized conductance peaks corresponding to the single- (0.0052 G_0), two- (0.011 G_0), and three- (0.016 G_0) molecule junction states were observed in the solution histogram by integrating 750 conductance traces. On the other hand, the conductance peaks corresponding to the single- and two-molecule junction states were observed at 0.0053 G_0 and 0.011 G_0, respectively, under vacuum conditions. It follows that in the case of the Au–[Ni(dmit)$_2$]$^-$–Au junction, single molecule conductance is independent of the measurement environment.

In summary, we evaluated the stability of Au single-atom contacts and single molecule conductance of [Ni(dmit)$_2$]$^-$ in both solution and vacuum using a nano-MCBJ. In a liquid environment, Au single-atom contacts had a lifetime of 1 s or more, and sufficient stability was acquired. The single molecule conductance of [Ni(dmit)$_2$]$^-$ is 0.0052 G_0, and was not dependent on the measurement environment. Currently, a study of the change in conductance of Ni(dmit)$_2$ by electrochemical oxidation–reduction is in progress.

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