Conductance of single 4,4'-bipyridine molecule anchored on Au electrodes under electrochemical potential control

Kunio Hashimoto [1], Manabu Kiguchi [*1,2], Tatsuya Konishi [1], Kei Murakoshi [1]

[1]Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan
[2]PRESTO, Japan Science and Technology Agency, Sapporo, 060-0810, Japan

Fax: 81-11-706-4811, e-mail: kiguti@sci.hokudai.ac.jp

We have investigated the conductance of a single 4,4'-bipyridine molecule anchored on Au electrodes under electrochemical potential control. Appearance of the peak in the conductance histogram suggests the formation of a single molecular junction. The conductance of the single 4,4'-bipyridine molecular junction was estimated from the peak value of 0.01 G_0 ($G_0=2e^2/h$) in the histogram. The conductance of the molecular junction did not change with the electrochemical potential. On the other hand, the intensity of the 0.01 G_0 peak in the conductance histogram decreased as the potential of the Au electrode scanned from 0.2 V to -0.4 V vs. Ag/AgCl. The electrochemical potential dependence of the intensity of the peak in the conductance histogram could be explained by the change in the adsorption properties of 4,4'-bipyridine on the Au electrode.

Key words: single molecular junction, electrochemical potential, bipyridine, conductance quantization

1. INTRODUCTION

Because of the technological potential for creating nano scale electronics devices, a single molecular junction, in which a single molecule is anchored on metal electrodes, has attracted wide attention. A variety of single molecular junctions have been fabricated with a scanning tunneling microscope (STM) or mechanically controllable break junctions (MCBJ) in ultra high vacuum, air, and solution [1,2]. In particular, there is considerable interest in single molecular junctions under the electrochemical potential control. The electrochemical potential determines the potential energy of the electrons of the metal electrodes, resulting in a shift of the molecular energy level to the Fermi level, and controls the interaction of the metals with molecules of the surrounding medium [3-6]. These characterstics could make it possible to prepare stable molecular junctions and to control the conductance of the molecular junctions. There are some experimental challenges to controlling the conductance of the single molecular junctions by the electrochemical potential. Li *et al.* investigated the conductance of perylene tetracarboxylic diimide (PTCDI) derivatives anchored on Au electrodes in 0.1 M NaClO$_4$ solution. The conductance of the single PTCDI molecule increased by two orders of magnitude when the electrochemical potential of the Au electrode scanned from 0.2 V to -0.5 V vs. Ag/AgCl [4]. Control of the conductance of single molecular junctions has been reported for

other molecules, such as hepta-aniline and oligothiophene [5,6]. A significant increase in the conductance value was explained by close alignment of the Fermi levels to the molecular energy levels by changing the electrochemical potential of the electrodes. While the conductance of the single molecular junction could be controlled by the electrochemical potential, the conductance was very low (below 10^{-3} G_0 : $G_0=2e^2/h$). It is strongly desirable to fabricate single molecular junctions showing a higher conductance and whose conductance could be controlled by the electrochemical potential.

In the present study, we focused on 4,4'-bipyridine as the candidate of the unit for the single molecular junction for the following two reasons. First, the adsorption states of the 4,4'-bipyridine molecule on the Au electrode can be controlled by the electrochemical potential. The adsorption state of the 4,4'-bipyridine molecule on Au(111) has been investigated using STM, infrared absorption spectroscopy (IRAS), and cyclic voltammogram [7]. The 4,4'-bipyridine molecule densely adsorbs on Au(111) with its molecular long axis perpendicular to the Au surface when the electrochemical potential of the Au electrode is maintained at -0.1~0.2 V vs. Ag/AgCl. As the potential scans to negative, the surface coverage decreases and the molecular long axis tilts with respect to surface normal. The conductance of the single molecular junction depends on not only the energy difference between the LUMO (or HOMO) and Fermi levels,

but also the configuration of the molecule at the junction [1]. Since the adsorption state (orientation, coverage) of 4,4'-bipyridine on Au(111) electrodes varies with the electrochemical potential, the conductance of the single 4,4'-bipyridine molecular junction is expected to be changed by the electrochemical potential. Second, the single 4,4'-bipyridine molecular junction may show high conductance. The conductance of the single 4,4'-bipyridine molecule anchored on Au electrodes was investigated in 0.1M NaClO₄ solution. The conductance was 0.01 G_0 [8]. This conductance value was the highest among the single molecular junctions reported before [1]. Although the electrochemical potential dependence of the conductance of the single 4,4'-bipyridine molecular junction is attractive, it was not investigated in detail at present. In the present study, we have investigated the single 4,4'-bipyridine molecule anchored on the Au electrodes under the electrochemical potential control. The conductance and probability of the formation of the single molecular junction were discussed by analyzing the conductance traces and conductance histograms observed during the stretching.

2. EXPERIMENTAL

The experiments were performed with a modified STM (Pico-SPM, Molecular Imaging) with a Nano ScopeIIIa controller (Digital Instruments). The STM tip was made of a Au wire (diameter ~0.25 mm, >99 %) coated with wax to eliminate ionic conduction. The Au(111) substrate was prepared by a flame annealing and quenching method. Figure 1 shows a schematic view of the experimental setup. The electrochemical potential (Φ) of the Au tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging) with a Ag/AgCl reference electrode. A 0.50 mm diameter Pt wire was used as a counter electrode. The measurements were carried out in 0.1M NaClO₄
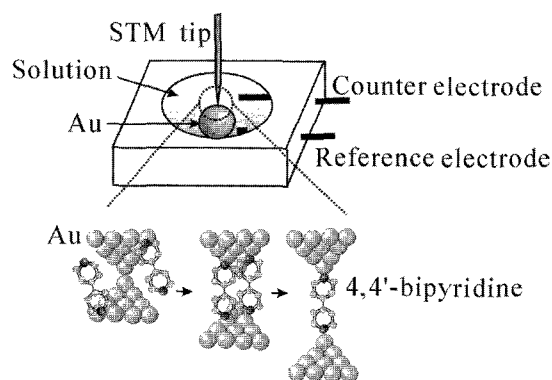

Fig. 1. Schematic view of the electrochemical STM. A single molecule is anchored on two Au electrodes during the stretching.

solution containing 1mM 4,4'-bipyridine. The STM tip was repeatedly moved into and out of contact with the Au substrate at a rate of 50 nm/s in the solution. Conductance was measured during the breaking process under an applied bias of 20 mV between the tip and substrate. All statistical data was obtained from a large number (over 1000) of individual conductance traces.

3. RESULTS AND DISCUSSION

Figure 2 shows the typical conductance traces of Au contacts broken in the 0.1M NaClO₄ solution containing 1 mM of 4,4'-bipyridine when the electrochemical potential of the Au contact was maintained at Φ= 0.2 V. The conductance decreased in a stepwise fashion, and the conductance value of the last plateau was 1 G_0 (see Fig. 2(a)), which corresponded to a single Au mono atomic contact [3]. After breaking the Au mono atomic contact, the conductance decreased in a stepwise fashion, with each step occurring at an integer multiple of 0.01 G_0 (see Fig. 2(b)). The conductance value of the last plateau was 0.01 G_0. The corresponding histogram shows a feature at 0.01 G_0 (Fig. 3(a)). In the absence of 4,4'-bipyridine, neither steps nor peaks were observed in the same conductance regime (Fig.
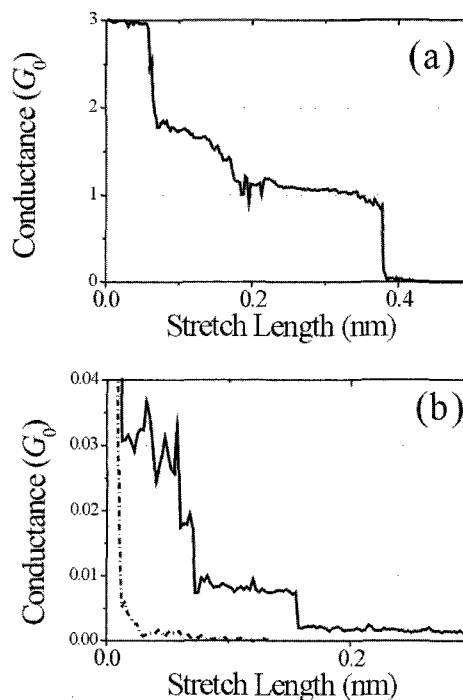

Fig. 2. (a) Typical conductance trace of Au contacts while breaking the contact in a 0.1 M NaClO₄ solution containing 4,4'-bipyridine. The electrochemical potential was Φ= 0.2 V. The dotted-line shows the result in the absence of molecules. (b) Zoom in of around 0.4 nm in (a).
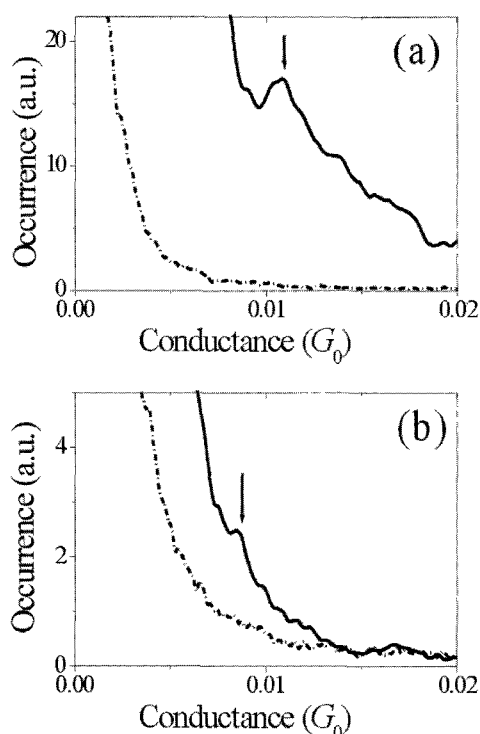
Fig. 3. Conductance histogram of Au contacts while breaking the contact in a 0.1 M $NaClO_4$ solution containing 4,4'-bipyridine. The electrochemical potential was (a) Φ= 0.2 V and (b) Φ= -0.4 V. The dotted-line shows the result in the absence of molecules.

2(b), Fig. 3). The steps in the conductance trace likely originate from the formation of a stable single 4,4'-bipyridine molecular junction. The conductance of the single 4,4'-bipyridine molecular junction was determined to be 0.01 G_0. This value agrees with the previously reported conductance value [8]. Figure 3(b) shows the conductance histogram of Au contacts at Φ= -0.4 V. The conductance value of the peak in the histogram was 0.01 G_0, and it did not change with

the electrochemical potential. On the other hand, the intensity of the 0.01 G_0 peak was smaller than that at Φ= 0.2 V.

The conductance of the single 4,4'-bipyridine molecular junction is discussed based on the previously reported experimental results of adsorption properties of 4,4'-bipyridine on Au(111) electrode [7]. First, the intensity of the 0.01 G_0 peak in the conductance histogram is discussed. The intensity of the 0.01 G_0 peak decreased as the electrochemical potential scanned to negative potential. As discussed in the introduction, the surface coverage of 4,4'-bipyridine varies with the electrochemical potential. When the electrochemical potential of Au(111) is maintained at Φ= -0.1~0.2 V, densely packed mono layer of 4,4'-bipyridine forms on Au surface. The surface concentration was estimated to be 6.9×10^{-10}mol cm^{-2}. As the potential scanned to Φ= -0.4 V, the surface concentration decreases to 3.4×10^{-10}mol cm^{-2}. Here, the formation process of the molecular junction is considered. At Φ= 0.2 V, the surface concentration of 4,4'-bipyridine molecules is large, and thus, a large number of molecules could be present near the Au contact before breaking the Au contact (see Fig. 4(a)). Therefore, the molecules could easily diffuse to the Au nano gap and anchor to the Au electrodes after breaking the contact. At Φ= -0.4 V, the surface concentration of 4,4'-bipyridine molecules is small, and the number of molecules near the Au contact would be small (see Fig. 4(b)). Therefore, the molecule would hardly diffuse to the Au nano gap for the formation of the junction after breaking the contact. The decrease in the probability of the formation of a single molecular junction could explain the experimental results that the 0.01 G_0 peak, which originated from the single 4,4'-bipyridine molecular junction, was smaller at Φ= -0.4 V than at Φ= 0.2 V.

The electrochemical dependence of the conductance histogram of the single 4,4'-bipyridine molecular junction is discussed. The conductance of the molecular junction did not change with the electrochemical potential, while
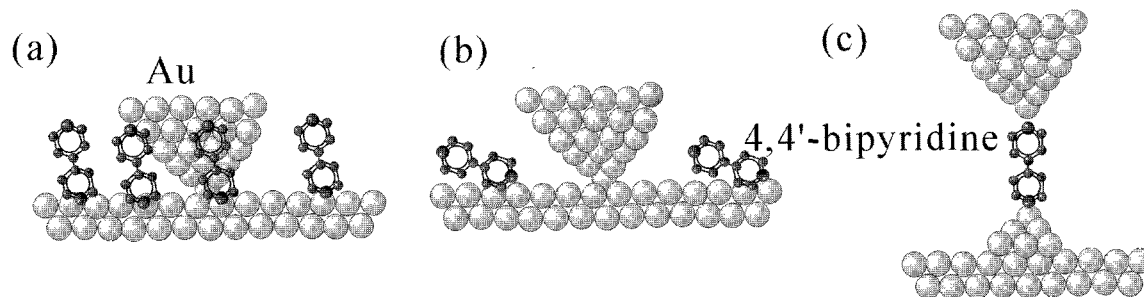

Fig. 4. Schematic view of the Au contact in the solution containing 4,4'-bipyridine. (a) The 4,4'-bipyridine molecules adsorb onto the Au with their long axis perpendicular to the surface at Φ= 0.2 V. A large number of molecules are present near the metal contact. (b) The 4,4'-bipyridine molecules adsorb with their molecular long axis tilted with respect to surface normal at Φ=-0.4 V. The surface concentration of 4,4'-bipyridine molecules is small. (c) Single bipyridine molecular bridge.

the intensity of the 0.01 G_0 peak varied with the electrochemical potential. The conductance of the single molecular junction depends on the energy difference between the LUMO (or HOMO) and Fermi levels and the atomic configuration of the molecular junction [1]. In terms of energy alignment, 4,4'-bipyridine could not be oxidized or reduced by the electrochemical potential in the present experimental condition (Φ= -0.4 ~ 0.2 V). The redox potential of 4,4'-bipyridine is Φ= -1.91 V [9]. Therefore, the energy difference between the LUMO (or HOMO) and Fermi levels would not largely change by the electrochemical potential in the present experimental condition. In terms of the atomic configuration of the molecular junction, the formation process of the single molecular junction is discussed. The single molecular junction is formed during the stretching of the Au electrodes [10,11]. Therefore, the molecule would be stretched between the Au electrodes once the single molecular junction is formed. The 4,4'-bipyridine molecule would anchor on the Au electrodes with an in-line configuration (see Fig. 4(c)). This configuration would be the same for the molecular junction at respective electrochemical potentials. Since the energy difference between the LUMO (or HOMO) and Fermi levels and the atomic configuration of the molecular junction would not largely change with the electrochemical potential [1], the conductance of the single 4,4'-bipyridine molecular junction did not change with the potential.

4. SUMMARY

We have investigated the conductance of a single 4,4'-bipyridine molecule anchored on Au electrodes in 0.1 M $NaClO_4$ solution containing 1mM 4,4'-bipyridine under the electrochemical potential. control. The conductance of the single 4,4'-bipyridine molecular junction was 0.01 G_0 . Although the conductance value did not change with the potential, the intensity of the 0.01 G_0 peak in the conductance histogram decreased as the potential scanned from Φ= 0.2 V to Φ= -0.4 V. This result suggests that the probability of the formation of the single molecular junction was smaller at the negative potential. The change in the conductance and the probability of the formation of the molecular junction could be explained by the molecular adsorption properties of 4,4'-bipyridine on the Au electrode.

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