Conductance of single 1,4-disubstituted benzene molecules anchored to Pt electrodes

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The authors have studied the conductance of a 1,4-disubstituted isocyanide (−NC) or thiol (−SH) benzene molecule anchored to two Pt electrodes. A single molecular junction showing a well-defined conductance value (≈3 × 10−2 G0, G0=2e2/h) was fabricated with the Pt electrodes. The conductance of the molecular junction was one order higher than the previously documented value using Au electrodes. These observations could be explained by differences in the local density of states of the contact metal atom at the Fermi level and the extent of the hybridization and energy difference between the molecular and metal orbitals. Further insight into the binding strengths of the metal-anchoring group bond was obtained by statistically analyzing the stretching length of the molecular junction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2757592]

There is a growing interest in the electron transport properties through single molecules due to their potential use in ultrasmall electronic devices.1 In studying the electron transport properties through a single molecule, it is important to design an appropriate molecule-electrode contact, since the contact plays a decisive role on the electron transport process through the molecule. Conductance measurements have been investigated for various single molecules using scanning tunneling microscope (STM) and mechanically controllable break junctions.1–3 In most of the studies, the Au–S bond is used to connect molecules to metal electrodes because stable molecular junctions can be easily obtained with this Au–S covalent bond. On the other hand, the conductance of a single molecular junction depends on the extent of the hybridization and energy difference between the molecular and metal orbitals and the local density of states (LDOS) ρ of the contact metal atoms at the Fermi level EF.4 An effective hybridization and a small energy difference between the molecular and metal orbitals, and also large ρ of the contact metal atom at EF are essential for the molecular junction to achieve high conductivity. Generally, the energy of the molecular orbital varies, depending on the molecule and its anchoring group. The ρ of Au is relatively low compared with other d-orbital metals at EF because of their sp2 state characteristics. Therefore, the Au–S bond is not always the best anchoring group for the single molecular junction showing high conductivity. It is important to develop a pair of metal and anchoring group other than Au–S to establish highly conductive single molecular junctions.

In developing anchoring groups, the conductance of single molecules anchored by isocyanide (−NC),5 carboxylic acid (−COOH)6 or amine (−NH2)7 (Ref. 7) anchoring groups to Au electrodes has been studied. Still, the metal of the electrode is restricted to Au. In spite of the variation in the choice of molecules, there have been few studies of single molecular junctions using metals other than Au. Among various metals, we pay attention to Pt for the following three reasons. First, Pt is chemically stable, which is essential for preparing a clean surface on the metal electrodes. Second, air stable thiol and isocyanide self-assembled monolayer (SAM) films are formed on Pt surfaces.8 The formation of stable SAMs indicates that the stable Pt–S or Pt–CN bond is formed and molecules are not decomposed on a Pt surface. Third, the ρ is high for Pt compared with Au at EF, since a narrow 5d band is located at EF for Pt.9 The conductance of a single molecule anchored to the Pt electrodes would be higher than that of the Au electrodes due to the high ρ of Pt. Recent theoretical calculations show promise for high conductivity of the molecular junctions with Pt electrodes.10,11 The calculated conductance of the molecular junction binding a benzene molecule to Pt electrodes by thiol or isocyanide coordination was estimated to be one order higher than that of the Au electrodes.10,11

In the present study, the effect of the metal and anchoring group on the conductance of single molecular junctions was investigated for 1,4-disubstituted (−NC− or −S) benzene molecules anchored to two Pt or Au electrodes. The metal-anchoring group bond strength was qualitatively estimated by the distance over which the molecular junction was stretched before breakdown. The conductance of the single molecular junction is discussed, considering a simple tunneling model.

The experimental design used in this study was the same as described in our previous report.5 A sharp tip was used, comprising a Pt wire (diameter of ∼0.25 mm, >99.9%). The substrate was Pt(111), prepared by flame annealing and quenching method.12 The measurements were carried out in tetrathynylglycol dimethyl ether (tetraglyme). The solution contained 1 mM 1,4-disocyanobenzene and 1,4-benzenedithio. A STM tip was repeatedly moved into and out of contact with a metal substrate at a rate of 50 nm/s in the solution. Respective molecules terminated into and out of contact with the substrate electrodes at a rate of 50 nm/s in the solution. Respective molecules terminated into and out of contact with the substrate electrodes 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 were obtained from a large number (over 1000) of individual conductance traces. Figures 1 and 2 show the typical conductance traces and histograms of the Pt contacts during breaking the contact in a tetraglyme solution, with and without 1 mM 1,4-diisocyanobenzene or 1,4-benzenedithiol. In the absence of molecules, neither plateaus nor peaks were observed both in the conductance traces and histograms (see Figs. 1 and 2). In solution containing the molecules, there are two characteristics in the conductance traces. First, the conductance trace shows a conductance fluctuation, which would originate from the structural transformation of the molecular junction. Second, the trace shows a plateau in which the conductance is nearly constant. The corresponding histogram shows a feature at $3 \times 10^{-2} G_0$ [see Figs. 2(a) and 2(b)]. The last plateau before the contact is broken in the conductance trace and a peak observed in the conductance histogram likely originates from the formation of single Pt/1,4-diisocyanobenzene/Pt and Pt/1,4-benzenedithiol/Pt junctions. The conductance of a single molecular junction was determined to be $3 \times 10^{-2} \pm 10^{-2} G_0$ for both molecular junctions. A benzene molecule is possibly bound to Pt atoms via S atoms for the Pt/1,4-benzenedithiol/Pt junction. For the Pt/1,4-diisocyanobenzene/Pt junction, isocyanide coordination via C atoms may contribute to the junction formation. In the following, these molecular junctions are referred to as the molecular junction with the Pt–CN bond and the molecular junction with the Pt–S bond, respectively. In our previous study, the conductance of the molecular junction was determined to be $4 \times 10^{-3} \pm 10^{-3} G_0$ for the Pt–CN bond, respectively. In our previous study, the conductance of the molecular junction was determined to be $4 \times 10^{-3} \pm 10^{-3} G_0$ for the Pt–CN bond, respectively. In our previous study, the conductance of the molecular junction was determined to be $4 \times 10^{-3} \pm 10^{-3} G_0$ for the Pt–CN bond, respectively. In our previous study, the conductance of the molecular junction was determined to be $4 \times 10^{-3} \pm 10^{-3} G_0$ for the Pt–CN bond, respectively. In our previous study, the conductance of the molecular junction was determined to be $4 \times 10^{-3} \pm 10^{-3} G_0$ for the Pt–CN bond, respectively.

Before discussing the conductance of the single molecular junction in detail, the metal-anchoring group bond strength is discussed by statistical analysis of the conductance trace. Since the last plateau corresponds to a single molecular junction, the length of the last plateau should be the distance over which the single molecular junction can be stretched before breakdown (breakdown distance). The breakdown distance reflects the stability of the molecular junction and the strength of the metal-anchoring group bond. To evaluate characteristics of the breakdown distance quantitatively, the distribution of the breakdown distance of the molecular junction was investigated (Fig. 3). For comparison, the results obtained by the Au–S and Au–CN bonds in our previous reports are also shown in the figure. The average length of the molecular junction was $0.16 \pm 0.02$ nm for the junction with the Pt–S bond, $0.11 \pm 0.01$ nm for the Pt–CN bond, $0.090 \pm 0.009$ for the Au–S bond, and $0.064 \pm 0.006$ nm for the Au–CN bond. Since the stretching length reflects the bond strength of the molecular junctions, the present results suggest that the strength of the metal-anchoring group bond decreased in the order of Pt–S, Pt–CN, Au–S, and Au–CN.

Based on the above experimental results, the conductance of the single molecular junction will now be discussed. The experimentally obtained conductance values of a single molecular junction can differ by two orders of magnitude among various reports, even for the same molecule, due to different experimental conditions. Generally, it is difficult to compare the conductance of single molecular junctions.
The present experimental study clearly showed that $\rho$, $\beta$, and $E_{F} - \varepsilon_i$ play the decisive role in determining the conductance of the single molecule. In developing an electronic device with a single molecule, it is becoming important to study electron transport through a single molecule with a high degree of functionality. The three factors depend on the choice of the molecules and the electrode metals. By considering these three factors in choosing the best electrode metal for the individual molecules, the conductance of the single molecule junction would be drastically improved, which leads to a higher performance for the molecular devices. Finally, the effect of the catalytic behavior of Pt on the single molecular junction is briefly discussed. Various catalytic reactions occur on the Pt surface due to its high catalytic reactivity. If an organic molecule is adsorbed strongly in an uncontrolled manner on the Pt electrode, the molecule cannot be used for the single molecular junction. On the other hand, by introducing the anchoring groups to the target molecule, the molecule is bound to the metal surface via the anchoring group. The molecule is in contact with the metal surface having well-defined adsorbed structure. Choosing appropriate anchoring group should be very important to control the adsorption of the molecule for the single molecular junctions.

In conclusion, we fabricated well-defined molecular junctions with Pt–S and Pt–CN bonds. The conductance of the molecular junctions with the Pt electrodes was one order higher than that with the Au electrodes. A Pt metal is a promising choice for a single molecular junction.

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