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Highly conductive single molecular junctions by direct binding of π-conjugated molecule to metal electrodes

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ABSTRACT

We have investigated electrical conductance of the single C_{60} and benzene molecules bridging between metal electrodes. The single C_{60} and benzene molecular junctions were prepared in ultra high vacuum. The single molecular junctions showed the high conductance values (around 0.1–1 G_0: $G_0 = 2e^2/h$), which were comparable to that of the metal atomic contact. The highly conductive single molecular junctions could be prepared by direct binding of the π-conjugated organic molecule to the metal electrodes without the use of anchoring groups. For comparison, the single 1,4-benzenediamine molecular junction was investigated in solution. The benzene molecule was bound to the Au electrodes via amine (anchoring group) for the single 1,4-benzenediamine molecular junction. The conductance of the single 1,4-benzenediamine molecular junction was $8 \times 10^{-3} G_0$. It was suggested that the anchoring groups acted as resistive spacers between the molecule and metal.

1. Introduction

The use of single molecules as functional devices is the ultimate end of the miniaturization of electronic circuits. To this end, various single molecular junctions were investigated using scanning tunneling microscope (STM), mechanically controllable break junction (MCBJ), and other techniques [1–3]. In most of the studies, the Au–S bond has been used to connect molecules to metal electrodes, because stable molecular junctions can be easily obtained with this Au–S covalent bond. In the simple tunneling model, the conductance of a single molecular junction depends on the extent of the hybridization and energy difference between the molecular and metal orbitals, the local density of states (ρ: LDOS) of the contact metal atoms at the Fermi level, and the degree of π-conjugation [4]. An effective hybridization and a small energy difference between the molecular and metal orbitals, large ρ of the contact metal atom and high degree of π-conjugation are essential for the single molecular junction to achieve high conductivity. Generally, the energy of the molecular orbital varies, depending on the molecule and its end group. The Au–S bond is not always the best metal-molecule bond for the single molecular junction showing high conductivity. It is important to develop metal-molecule bonds other than Au–S bond to establish highly conductive single molecular junctions.

In developing metal-molecule bonds for the single molecular junctions, various anchoring groups (e.g. isocyanide (–NC), carboxylic acid (–COOH), amine ($-NH_2$)) and metal electrodes (e.g. Au, Ag, Pt) have been investigated [5–9]. In the case of the single 1,4-disubstituted benzene molecular junction, its conductance could be increased by changing the metal-molecule bond from typical Au–S bond to Pt–S or Pt–CN bonds [8]. However, the conductance value was still smaller than that of the metal atomic contact. One of the possible approaches to improve the conductance of the single molecular junction is the direct binding of π-conjugated molecule to the metal electrodes without the use of anchoring groups. Here, we pay attention to the single C_{60} and benzene molecules bridging between metal electrodes. C_{60} and benzene are highly π-conjugated molecules whose conducting orbital (HOMO or LUMO) is the fully delocalized π-orbital. Therefore, the high conductance values could be expected for the single C_{60} and benzene molecular junctions, if these π-conjugated molecules could be directly bound to the metal electrodes.

In the present study, we have investigated the conductance of the single C_{60} molecule bridging between Au electrodes (see Fig. 1(a)) and benzene molecule bridging between Pt electrodes (Fig. 1(b)). For comparison, we have investigated the conductance of the single 1,4-benzenediamine molecule bridging between Au electrodes (Fig. 1(c)). The conductance of the single molecular junctions with and without anchoring groups was discussed by considering the π-conjugation of the single molecular junction.

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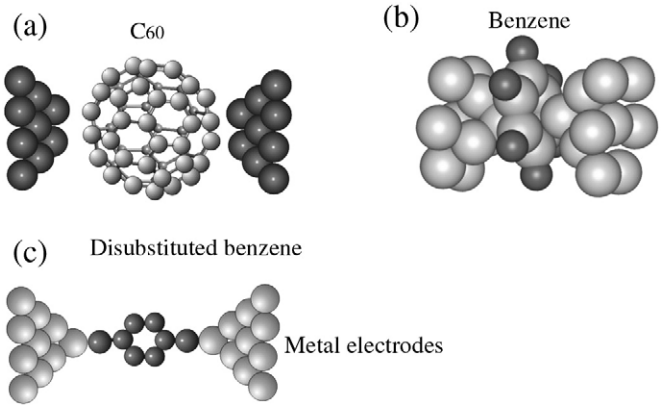

Fig. 1. Schematic view of single (a) C_{60}, (b) benzene and (c) disubstituted benzene molecular junction investigated in this study.

2. Experimental

The single C_{60} and benzene molecular junctions were fabricated in ultra high vacuum (UHV) chamber equipped with the MCBJ system. Fig. 2(a) shows the schematic view of the MCBJ system [10]. A notched metal wire (0.1 mm in diameter, 10 mm in length) was fixed with epoxy adhesive (Stycast 2850FT) on top of a bending beam. The beam was mounted in a three-point bending configuration. In UHV, the wire was broken by the mechanical bending of the substrate, and clean fracture surfaces were exposed. The bending could be relaxed to form the atomic-sized contacts between the wire ends using a piezo element for fine adjustment. The C_{60} was deposited on the Au nano contacts with a Knudsen cell. The amount of deposited C_{60} was monitored with a thickness monitor. Benzene was introduced to the Pt nano contacts using a leak valve via a heated capillary.

The single 1,4-benzenediamine molecular junction was fabricated in solution with modified electrochemical-STM (EC-STM) system. Fig. 2(b) shows the schematic view of the EC-STM system [11,12]. The STM tip was made of a Au wire (diameter ~0.25 mm, >99 %) coated with wax to eliminate ionic conduction. The substrate was Au(111), prepared by a flame annealing and quenching method. The electrochemical potential (Φ_0) of the Au tip and substrate was controlled using a potentiostat (Pico-Stat, Molecular Imaging Co.) with a Ag/AgCl reference electrode. A 0.50 mm diameter Pt wire was used as a counter electrode. The electrolyte was 0.1 M NaOH containing 1 mM 1,4 benzendediamine. An STM tip was repeatedly moved into and out of contact with a metal 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.

3. Result

3.1. Single molecular junction without anchoring groups

Fig. 3 shows typical conductance traces and histograms of the clean Au contacts before and after the introduction of C_{60}. The conductance was measured under an applied bias voltage of 300 mV between the electrodes. Before the introduction of C_{60}, the conductance decreased in a stepwise fashion, with each step occurring at integer multiples of G_0 ($G_0 = 2e^2/h$). The corresponding conductance histogram (Fig. 3(b)) showed a peak near 1 G_0, which corresponded to the clean Au atomic contact [11–13]. After the introduction of C_{60}, the trace showed a plateau in which the conductance was nearly constant (arrow in Fig. 3(a)), and the conductance value of the plateau was an integer multiple of 0.3 G_0. The corresponding conductance histogram showed a peak at 0.3 G_0 (arrow in Fig. 3(b)). Neither steps nor peaks were observed below 0.1 G_0 in the conductance trace and histogram. In the absence of C_{60}, neither steps nor peaks were observed in the same conductance regime. So, the appearance of the plateau at integer multiples of 0.3 G_0 in the conductance trace and a peak in the conductance histogram strongly suggested that the plateau in the trace and the peak in the histogram showing the values of $1\times$ and 2×0.3 G_0 could be ascribed to one and two C_{60} molecules, respectively. The conductance of the single Au/C_{60}/Au junction was determined to be $0.3(\pm 0.1)$ G_0 in UHV. This conductance value agreed with the previous reported value of 0.1 G_0–0.5 G_0 [14,15]. Here, it should be noticed that the conductance of the single Au/C_{60}/Au junction was discussed with a limited number of IV characteristics or conductance traces in the previous study. On the other hand, the conductance of the single Au/C_{60}/Au junctions was precisely determined by statistical analysis of the repeated measurements (more than 3000 times and five samples) in the present study. Under the same experimental conditions, the conductance of the single Ag/C_{60}/Ag junction was determined to be $0.5(\pm 0.1)$ G_0 [10]. The single C_{60} molecular junction showed the high conductance value which was comparable to that of a metal atomic contact.

The single Pt/benzene/Pt junction was investigated in UHV at 4 K [16]. The insert equipped with MCBJ was put into the liquid He container to cool the sample [17]. Measurements of conductance, vibration spectroscopy of a single molecular junction and shot noise, and theoretical calculation results revealed the formation of the single

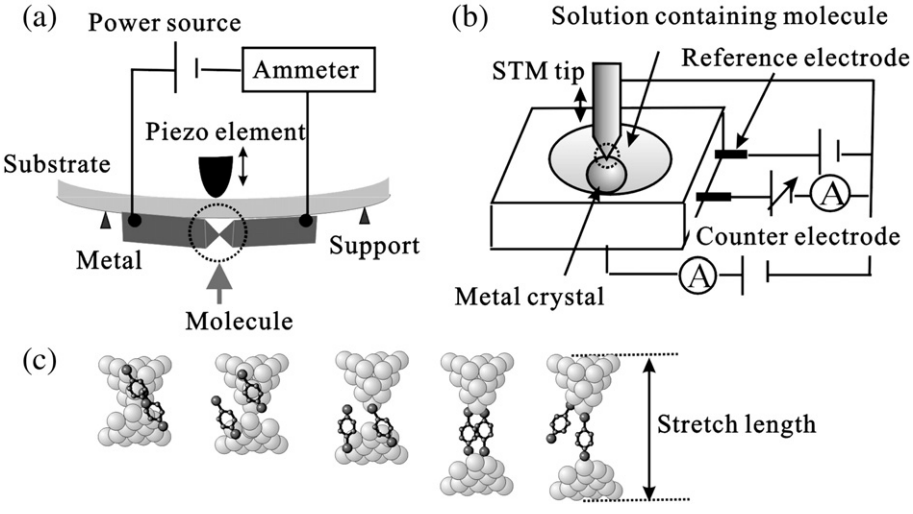

Fig. 2. (a) MCBJ system to investigate the single molecular junction in UHV. (b) EC-STM system to investigate the single molecular junction fabricated in solution. (c) Schematic view of the formation process of the single molecular junction during stretching the metal contact.