Photochemical Reaction Using Aminobenzenethiol Single Molecular Junction

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Photo-induced chemical reaction of p-aminobenzenethiol (ABT) was investigated using the lithographically fabricated mechanically controllable break junction (MCBJ). The ABT single-molecule junction was formed at the nanogap of the MCBJ and the formation was confirmed by the electronic transport measurement including current versus bias voltage characteristics. Light irradiation at the nanogap revealed that ABT molecules were subject to photo-induced dimerization, which was confirmed by measuring SERS spectrum. In addition, we tuned the gap size using MCBJ technique and demonstrated that the photo-induced dimerization was absent for the molecules at the wide gap. [DOI: 10.1380/ejssnt.2018.137]

Keywords: Surface enhanced Raman scattering; Single molecular junction; Photochemical reaction; Plasmon

I. INTRODUCTION

A plasmonic nanostructure generates an intense electromagnetic field, when it is excited by light at the resonant frequency [1, 2]. The plasmonic nanostructure together with the enhanced field has been used to various applications, such as nano sensing, photo catalysis, optical switching, optomagnetic devices, medical analysis, and so on [3-7]. Recently, a photo chemical reaction with plasmonic nanostructure has attracted wide attention, because useful photo chemical reaction can proceed with an unconventional weak light [8-12]. Two-photon chemical reaction, photo chemical reaction induced by hot electron or plasmon heating have been investigated for a variety of systems. Tsuboi et al. reported two-photon ring-opening photochronic reaction of a diarylethene (DE) derivative with the Au nano particles [9]. The two-photon reaction was induced by irradiation of near infrared laser light. The yield of the photochronic reaction was proportional to the square of the intensity of the light source, which explained the progression of the two-photon reaction. Adleman et al. reported the photo catalytic reaction, where CO2, CO and H2 gas was generated from the liquid mixture of ethanol and water over Au nanoparticles [10]. The plasmon heating of the nanoparticles provided the heat of the evolution reaction. Mukherjee et al. reported the plasmon induced dissociation of H2 on Au nanoparticles using visible light [11]. Surface plasmon excited in the Au nanoparticles decayed into hot electrons, which transferred into an H2 molecule, triggering dissociation. Although various photo chemical reactions with plasmonic nanostructures have been reported, the gap control still remains challenging. There are some experimental challenges to control the gap size with the nano fabrication techniques (e.g. lithographic technique, self-assembled monolayer technique) [13, 14]. However, it is still difficult to prepare the subnm scale with the conventional techniques.

Here, we report the photo chemical reaction at the tiny gap space, which gap space is smaller than the conventional nano-scale gap, for the single molecular junction. The formation of single molecular junction was confirmed by the electric resistance between the metal electrodes, and the progress of the photochemical reaction was monitored by the surface enhanced Raman scattering (SERS). Since the electric field was enhanced at the small gap, the photo chemical reaction at the gap was selectively investigated with SERS [15]. As the target reaction, we focused on the photo induced chemical transformation from p-aminobenzenethiol (ABT) to 4,4’-dimercaptoazobenzene (DMAB) [16-20]. The ABT is an important probe molecule in SERS, because of its strong interaction with Au or Ag surface, and the intense SERS signal. This photo induced chemical transformation (PICT) was observed during the SERS measurement, where ABT was gradually changed to DMAB upon continuous laser excitation. The PICT was induced by energy transfer from surface plasmon resonance to surface adsorbed ABT, and ABT was oxidized to DMAB [21]. The dependences of laser intensity, electrochemical potential, and pH of the solution have been investigated. Takeyasu et al. reported that the photo chemical reaction occurred

FIG. 1. (a) Scheme of photo dimerization of ABT into DMAB. (b) Experimental setup to study the photo dimerization in the single molecular junction.
with the laser intensity of 40 W/mm$^2$ on a highly uniform two dimensional Ag nano particle arrays $^{[22]}$. By controlling the distance between nano particles, the progression of the photochemical reaction should be controlled with a fixed laser intensity. In this study, here, we have investigated the photo induced chemical reaction of ABT with the mechanically break junction (MCBJ) techniques $^{[23]}$. The gap distance can be precisely controlled with the MCBJ setup. The reaction was investigated with SERS for different gap-distances. At the ABT single molecular junction, the photo induced chemical transformation occurred, while the reaction did not occur at the large gap. We could control the progression of photo chemical reaction by controlling the gap size.

II. EXPERIMENTAL

Figure 1(a) shows the scheme of target reaction in this study: photo dimerization of ABT. The ABT molecule is oxidized by photo irradiation, and it is dimerized into DMAB. Figure 1(b) shows the schematic view of the experimental setup to study the photo dimerization reaction of the ABT single molecular junction. The single molecular junction was prepared by breaking the Au nano electrode with MCBJ technique. For the SERS and conductance measurement, the Au electrode should be electrically insulated from the substrate, and the intensity of the Raman background scattering should be suppressed.

We, thus, prepared the Au nano electrodes as the following procedure [Fig. 2(a)]. An insulating SiO$_2$ film (1000 nm) was deposited on the polished phosphor bronze substrate (thickness: 0.5 mm) by means of sputtering [Fig. 2(a)I]. The SiO$_2$ layer provides electrical insulation and limits the intensity of the Raman background scattering. Over the oxide, a polyimide film was deposited with spin-coating [Fig. 2(a)II]. The Au electrode (size of the narrowest constriction 150 nm $\times$ 300 nm) was prepared using electron beam lithography [Fig. 2(a)III] and lift-off technique [Fig. 2(a)IV]. Metallic layers (Cr: 3 nm and Au: 130 nm) were thermally deposited on the substrate. Subsequently, the polyimide underneath the Au junctions was removed by isotropic reactive ion etching using O$_2$ plasma (power: 80 W) [Fig. 2(a)V]. Figure 2(b) shows the obtained free-standing Au nano-bridge on the substrate. Typical bridge length was in the range of 2 $\mu$m.

The Au electrode was mounted on the MCBJ setup [Fig. 1(b)]. A drop of an ABT solution (5 mM in EtOH) was provided onto the Au electrode surface before the junction was formed. The Au electrode was then disconnected by bending the substrate on a piezo stage (NEC tokin). The electrical measurements were performed using a Keithley 428 programmable amplifier. The SERS signals were collected using a NanoFinder30 Raman microscope (Tokyo Instruments) with a near-infrared laser ($\lambda_{\text{ex}} = 785$ nm, 100 mW) as an excitation light. The laser beam was focused onto the molecular junctions using an objective lens with 50$\times$ magnification and 0.95 numerical aperture. The irradiated area of the substrate was $\sim$1 $\mu$m$^2$, and the laser intensity was 50 kW/mm$^2$. All experiments were performed with five distinct samples.

III. RESULTS AND DISCUSSION

Continuous measurement of the conductance allows us to find formation of the ABT single molecular junction. Figure 3 shows the conductance change upon rupture of the junction. The conductance trace shows a step at 1 $G_0$($2e^2/h$), corresponding to the Au atomic junction $^{[24-26]}$. In the case of the Au atomic junction, a single channel of Au 6s contributes to electron transport, and the transmission of the channel is 100%. Therefore, the conductance of the Au atomic junction is 1 $G_0$ $^{[27]}$. Further measurement allows us to find formation of the ABT single molecular junction.
The current through a single conduction orbital, the charge transport is observed. When electron transport is supported by the current versus bias voltage (I-V) curve, the conductance decreases to low value around 0.106 eV. The previously reported STM-BJ measurement revealed the conductance of the ABT single molecular junction was 0.006 $G_0$ [28]. The 0.006 $G_0$ plateau indicates the formation of ABT single molecular junction. Finally, the conductance decreases to low value around 0.106 eV, corresponding to the breaking the junction. The formation of the ABT single molecular junction is supported by the current versus bias voltage (I-V) characteristics of the junction. Figure 4 shows the example of the I-V curve of the junction showing conductance of 0.006 $G_0$. The non-linear characteristic of molecular charge transport is observed. When electron transport through a single conduction orbital, the I-V curve of the single molecular junction is represented by

$$I(V) = \frac{2e}{h} \left[ \tan^{-1} \left( \frac{eV - 2\varepsilon_0}{2\Gamma} \right) + \tan^{-1} \left( \frac{eV + 2\varepsilon_0}{2\Gamma} \right) \right]$$

(1)

where $\varepsilon_0$ and $\Gamma$ are the energy difference between the conduction orbital and Fermi level of the metal electrode, and the coupling strength between the molecule and both metal electrodes [29-31]. By fitting the experimental data with Eq. (1), $\varepsilon_0$ and $\Gamma$ are determined to be $\varepsilon_0 = 0.65$ eV and $\Gamma = 0.06$ eV. The obtained values are close to the typical value of di-substituted benzene single molecular junction [31].

We then investigate the SERS of ABT single molecular junction. For comparison, the Raman spectrum of bulk ABT is shown in Fig. 5. The obtained Raman spectrum agrees with the previous study [32]. The Raman spectrum presents peaks at 309, 391, 453, 629, 810, 1011, 1078, 1167, 1269, and 1583 cm$^{-1}$, which can be assigned to C-H bending mode, C-C torsion mode, C-C stretching mode, C-C-C stretching mode, C-H wagging mode, C-C wagging + C-C-C stretching mode, C-S stretching mode, C-H bending mode, C-H stretching mode, and ring breathing mode, respectively. Figure 6 shows a photo image of Au nano gap electrode and the SERS signal of the different areas of the electrode. No SERS signal is detected on the SiO$_2$ layer (III). On the flat Au electrodes, weak SERS signal is observed at 1076, 1138, and 1585 cm$^{-1}$ (II), which agrees with the previously reported results with Au nano particles. The strong SERS signal is observed at the nano-gap between Au electrodes (I). The signal is strongly enhanced when the electric field of the light is parallel to the junction axis. These results indicate the signal is due largely to the localized surface plasmon excitation of the Au nano electrodes [33]. The SERS spectrum at the nano gap shows peaks at 1072, 1139, 1185, 1306, 1389, 1438, and 1580 cm$^{-1}$. The peaks at 1389 cm$^{-1}$ and 1438 cm$^{-1}$ modes are assigned to the N=N stretching mode of DMAB, and the peak at 1139 cm$^{-1}$ can be assigned to C-N stretching mode and C-H in-plane bending mode of DMAB. Although the peak at 1139 cm$^{-1}$ can be also assigned to b$_2$ mode of ABT [32], the appearance of peaks at 1389 cm$^{-1}$ and 1438 cm$^{-1}$ confirm the progression of the photo dimerization reaction of ATP. The 1389 cm$^{-1}$ and 1438 cm$^{-1}$ modes appear in SERS from the beginning (< 1 s). The appearance of 1139, 1389, and 1438 cm$^{-1}$ modes are observed for all five distinct samples, although the peak intensity of the modes varies with the sample. To obtain the SERS with high S/N ratios, the laser intensity of 50 kW/mm$^2$ and integration time of 1 s are minimum condition. The previous study of ABT molecules on Au or Ag nano particles shows that the photo dimerization reactions proceeds when the laser intensity is large (> 40 W/mm$^2$) [22]. The laser intensity is 50 kW/mm$^2$ in the present study. The progression of photo dimerization reactions under the current photon flux is consistent with the previous study [22]. Here, the conductance of the junction does not change by irradiation of light. Therefore, chemical reaction does not proceed for the bridging ABT molecule, but the surround-

![FIG. 4. Typical I-V curve observed for the ABT single molecular junction with a conductance value of 0.006 $G_0$ around 0 bias regime, and the I-V curve obtained by the single level tunneling fitting (with $\varepsilon_0 = 0.65$ eV, and $\Gamma = 0.06$ eV).](https://www.jstage.jst.go.jp/browse/ejssnt/)

![FIG. 5. Bulk Raman spectrum of the powder sample of ABT ($\lambda_{ex} = 785$ nm, 100 mW). The integration time is 1 s.](https://www.jstage.jst.go.jp/browse/ejssnt/)

![FIG. 6. (a) Photo image of the Au nano gap electrode. (b) SERS spectra collected from the nano-gap between Au electrodes (I), the surrounding SiO$_2$ layer (II), and the body of the Au electrodes (III).](https://www.jstage.jst.go.jp/browse/ejssnt/)
ing ABT molecules.

When light illuminates Au nano structure, the localized surface plasmon (LSP) is excited on the nano structure. The strong electromagnetic field is formed around the nano structure, and the range at which enhanced field extends, is about the size of nano structure. When the Au nano structure is approached to another Au nano structure, the LSP couples with each other, and the electromagnetic field intensity is strongly enhanced at the gap. Generally, there is some threshold strength of the electric field for triggering chemical reaction \[7\]. Although the electric field is the strongest at the center of the gap, the chemical reaction can occur at the position where the electric field is beyond the critical strength of the electric field. Actually, the previous study supports this idea. Ueno et al. investigated the plasmon assisted polymerization reaction of epoxy-based negative photo resist (SU-8) with the checkerboard pattern of nano blocks \[12\]. The size of nano blocks was 120 nm \(\times\) 120 nm and the gap size was 6 nm. The polymerized SU-8 was observed by SEM after irradiation of light. The electric field was enhanced in the nano gap, and the field intensity rapidly decreased with the distance from the center of the nano gap, but, the polymerized SU-8 was observed in an oval surrounding 30 nm.

Finally, we study the photo dimerization reaction for ABT with the large gap electrode. Figure 7 shows the SERS spectrum when the gap distance is as large as 4 \(\mu m\). Inset figure is the microscope image of the nano gap electrode. The SERS signal is observed at 1072 cm\(^{-1}\) and 1580 cm\(^{-1}\). The obtained SERS spectrum agrees with that of the flat electrode and previously reported results with Au nano particles. The 1389 cm\(^{-1}\) and 1438 cm\(^{-1}\) modes-characteristic of DMAB are not observed, indicating that the photo dimerization reaction does not occur for the large gap. This experimental result clearly shows the importance of the enhanced field caused by the plasmon coupling. Also, this result indicates that we can control the photochemical reaction by the gap size.

IV. CONCLUSION

We have investigated the photo induced chemical reaction of ABT with the single molecular junction. The ABT single molecular junction was fabricated using the MCBJ techniques. The formation of the single molecular junction was confirmed by the electrical conductance and \(I-V\) measurements. The 1389 cm\(^{-1}\) and 1438 cm\(^{-1}\) modes characteristic of DMAB were observed, indicating the progression of photo dimerization reaction. Meanwhile, the reaction did not occur at the large gap. We could control the progression of photo chemical reaction by controlling the gap size.

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