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Research Report

Nanocarbon materials synthesized by local probe chemistry

Shigeki Kawai

National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan
E-mail: KAWAI.Shigeki@nims.go.jp

Scanning probe microscopy has been used to characterize structures and electronic properties of surfaces as well as to construct nanostructures via atom-by atom manipulation. Recent advances in tip-functionalized scanning probe microscopy allow us to measure the inner structures of molecules. This bond-resolved imaging technique is of particular importance in the investigation of precursors and products during on-surface reactions. In this article, tip-induced structural isomerization and additional reactions will be discussed.

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1. Introduction

It has already been many years since the development of scanning tunneling microscopy (STM) [1] and atomic force microscopy (AFM) [2], and they are now deployed not only in surface science but also in various other fields, such as chemistry and biology. It is no exaggeration to say that they are one of the most important measurement methods that support today's nanoscience. These techniques, which use the tunneling current flowing between a probe and a surface and the generated force to produce images, can elucidate the structures and states of solid surfaces and adsorbates in real space and with high resolution. In addition, atoms and adsorbates on a surface can also be directly manipulated using a probe [3,4], resulting in the realization of the fabrication of nanoscale structures [5–7].

With the development of STM, research on molecules adsorbed onto solid-liquid interfaces and surfaces in ultra-high vacuum has been actively conducted [8,9]. In particular, experiments at the single-molecule level are possible at extremely low temperatures, and it became possible to observe molecular orbitals [10] and to measure their states using the inelastic tunneling currents [11] caused by the vibrational excitations of bonds. In recent years, a fusion with tip optical measurements [14,15] that combines probe-enhanced Raman spectroscopy [12,13], terahertz light, etc. has been developing [16]. Research on structural changes at the single-molecule level is also being actively conducted. Carbon nanostructures, such as novel compounds [17] and graphene nanoribbons (GNR) [18,19] can now be synthesized by chemical reactions of molecules deposited onto a metal surface by heating. In addition, highly reactive radical species were also synthesized by elimination reactions, which cuts off specific bonds in a molecule using the tunneling current flowing from a probe [20–23]. Isomerization using instabilities [24,25] and single-molecule synthesis by addition reactions that stabilize atoms and molecules have also been realized [26]. The measurement method for identifying the internal structure of a molecule using a probe terminated with a carbon monoxide (CO) molecule can be cited as the reason for the rapid development of this "local probe chemistry" field [27,28]. Syntheses that were difficult to carry out using conventional organic chemistry methods became possible by directly looking at the structure of one molecule and changing it using the tunneling currents with a CO probe. We have been engaged in research on surface chemistry using this ultra-high resolution probe microscope for 10 years [29–31]. In this paper, we will introduce the creation of direct nanomaterials by "local probe chemistry" recently carried out using a probe, and elemental technology.

2. Elemental technology

2.1 Molecular and atomic manipulation

Atomic-level pointed STM and AFM probes can be positioned horizontally (X, Y) and vertically (Z) with picometer-level accuracy for moving atoms and molecules mechanically or electrically [3]. There is a pulling mode and a pushing mode for mechanical movements, and they can be modulated and judged based on the tunneling current and the modulation of the signal in the Z direction [32]. In addition, not only horizontal movements are possible but this method can also be used to pick up and drop atoms and molecules adsorbed onto a surface. In contrast, if an object consists only of molecules, it is possible to move it using the excitations of bonds and the tunneling currents and the interactions between dipoles of the molecule and the electric field from the probe [33].

In addition, intramolecular bonds can also be broken by the tunneling current flowing between the probe and the sample and applying a bias voltage greater than a certain value [20]. So far, cleavages of C–H bonds, C–Br bonds, C=O bonds, etc. have been realized. Breaking a bond yields highly reactive radicals with unpaired electrons [21]. Molecular manipulation by isomerization using this instability is also possible [24,25].

By making full use of these atomic and molecular manipulations, "local probe chemistry," such as the rearrangement of single molecules, the cleavage of bonds and isomerization can be performed.

2.2 Intramolecular structure observation

In non-contact AFM, the resonance frequency that changes depending on the force acting between the probe of the force sensor and the sample is used as a signal [34]. In addition to long-range forces, such as the van der Waals force and electrostatic forces, the interactions forces include a chemical bond force, which is a short-range force that provides atomic resolution. Short-range forces, as expressed by the Lennard-Jones potential, decrease with the 6th power for the force of attraction and with the 12th power for the force of repulsion

with respect to distance. The distance dependence of a repulsive force is stronger than that of an attractive force, which leads to a higher resolution. In contrast, as a probe is terminated by atoms of the substrate in normal observations, a probe with a sharp tip is more active than a substrate with a stable crystal plane. Due to this high reactivity, the atoms at the tip of the probe move irregularly with a large attractive force before reaching the repulsive force region, making stable imaging difficult. Especially in the case of observing molecules adsorbed onto the surface of a substrate, the adsorption energy to the probe is higher than the adsorption energy to the substrate, and unintended molecular manipulation occurs frequently [35].

In 2009, a measurement method using a probe terminated with a CO molecule was proposed [27]. The reactivity of a CO probe is low, and stable imaging is possible in the repulsive region. In addition, by tilting the CO probe in the *XY* direction with the interaction force, the total charge density derived from the bond is very localized and can be detected. As a result, intramolecular bonds could be clearly imaged similar to as if drawing a structural formula [36]. Even in STM, it has been reported that a similar contrast can be obtained by terminating the probe with a CO molecule or something similar [28].

3. Local chemical reactions using a probe

In this section, we will introduce research on structure identification by high-resolution observations of compounds obtained by the radicalization of molecules and subsequent isomerization. We can do this by making full use of the above-mentioned manipulation of atoms and molecules, and addition reactions, in which different elements and molecules are joined to radicals with a probe.

3.1 Isomerization by elimination reaction

In this study, we aimed to perform the single-molecule synthesis of Sondheimer–Wong diyne, which was organically synthesized by Wong et al. in 1974 [37]. The diyne molecule has a distorted triple bond (Fig. 1(a)), which is why it is highly reactive. In organic synthesis, it is used to synthesize a more stable pentalene molecule fused with a five-membered ring. In this study, the reverse reaction was performed by a probe.

With pentalene as the nucleus and naphthalene at both ends thereof, a precursor molecule substituted with bromine atoms at positions 6 and 13 of the five-membered ring was used (Fig. 1(b)). High-purity molecules obtained by organic synthesis were placed in a crucible and adsorbed onto a clean Cu(111) substrate by heat sublimation under ultra-high vacuum. When the temperature of the substrate reached room temperature (20 °C), the C–Br bond was broken due to the catalytic effect of Cu. Therefore, the temperature of the substrate was maintained at about 20 K for the adsorption of the molecules. Figure 2(a) is an STM topographic image of the precursor molecule adsorbed onto the substrate. The molecule indicated by the arrow is the reactant, and when magnified, an asymmetric contrast derived from bromine was observed (Fig. 2(b)). Next, cleavage of the C–Br bond using the tunneling current was attempted. After positioning the probe on the red mark, the control between the probe and the sample was turned off, and further, the bias voltage was swept from 0 V to a positive value while measuring the tunneling current. Above 2 V, the tunneling current suddenly decreased (Fig. 2(c)). After that, when STM observation was performed, the bromine atom was desorbed, and a dented contrast was observed instead (Fig. 2(d)). Furthermore, another bromine atom was also removed similarly (Figs. 2(e) and 2(f)). Synthesis of radicals with unpaired electrons can be expected from this elimination reaction. However, when the structure was examined using an STM simulation image based on DFT calculations, it was found that the carbon bonded to bromine is stabilized by bonding with the Cu atom on the surface of the substrate. Therefore, it was found that diyne, the target compound, could not be synthesized on Cu(111).

Next, molecules were deposited onto a two-layer NaCl thin film to prevent stabilization with the Cu surface. The white

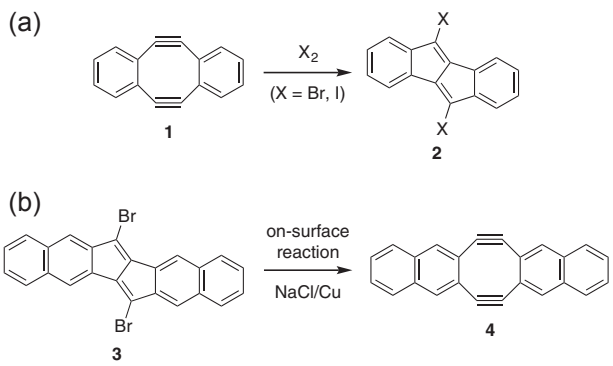

Fig. 1. (a) Sondheimer-Wong diyne **1** and pentalene derivative **2**. (b) Precursor molecule **3** for local probe chemistry and its product **4**.

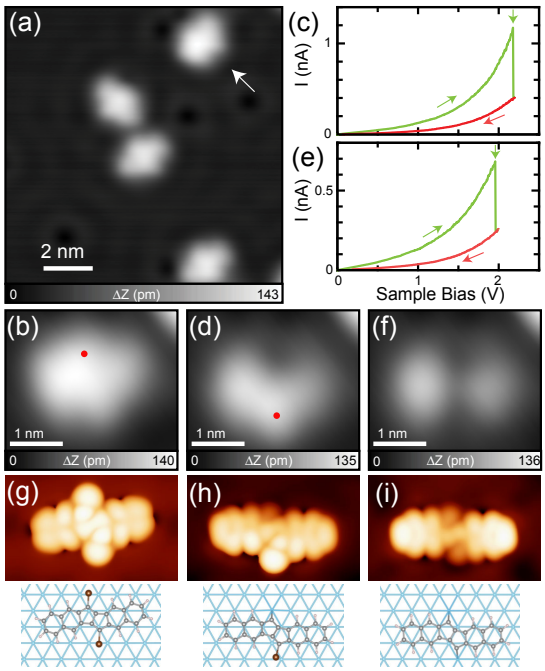

Fig. 2. (a) STM topography of the precursor molecules adsorbed on Cu(111) and (b) the close-up view. (c) *I*–*V* curve measured during the debromination reaction. (d) STM topography after the debromination. (e) *I*–*V* curves measured during the second debromination reaction. (f) STM topography after the second debromination. (g–i) Simulated STM topographies and their adsorption geometries.

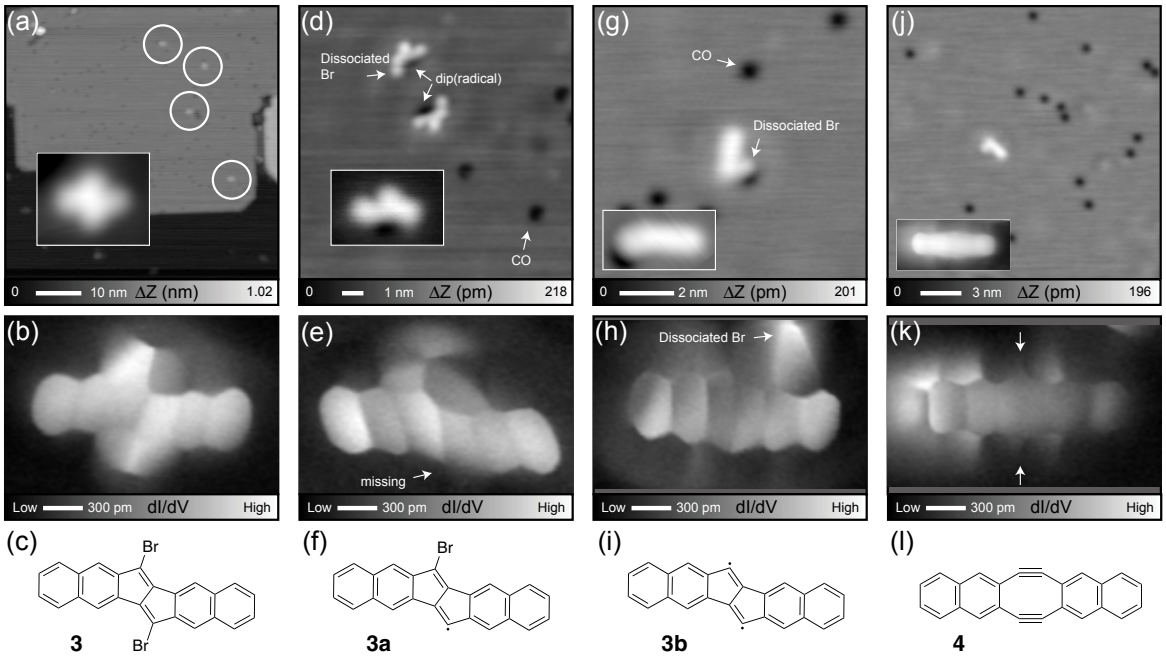

Fig. 3. (a) STM topography of the molecule adsorbed on a thin NaCl film. (b) High-resolution image taken with a CO terminated tip and (c) the corresponding chemical structure. (d) STM topography of the molecule taken after the first denomination. (e) High-resolution image and (f) the corresponding chemical structure. (g) STM topography of the molecule after the second debromination. (h) High-resolution image and (i) the corresponding chemical structure. (j) STM topography of another product, (k) the corresponding high-resolution image, and (l) the chemical structure.

circles in Fig. 3(a) indicate single molecules. In order to directly observe the structure, the tip of a probe was terminated with a CO molecule, and an dI/dV image was acquired at a constant height. As shown in Figs. 3(b) and 3(c), the contrast reflected in the structure of the precursor molecule could be obtained. Next, the probe was moved over the C–Br bond, and the bias voltage was gradually increased, similar as shown in Figs. 2(c) and 2(e). When the tunneling current decreased, the voltage returned and STM observation was performed (Fig. 3(d)). At that point, precursor molecules, which used to have a cross-shaped contrast, became a bent line. The probe was terminated again with a CO molecule and the structure was observed (Fig. 3(e)). As a result, it was found that the two C–Br bonds had been reduced to one (Fig. 3(f)). The remaining C–Br bonds could also be broken by a similar sweeping of the voltage. Subsequent observations confirmed two types of molecules. One is a slightly bent structure (Fig. 3(g)) and the other is a completely straight-line structure (Fig. 3(j)). High-resolution observations of these structures revealed that both bromine atoms were detached. Analysis focusing on the axis of the naphthalene site revealed that the original pentalene skeleton remained in the bent molecule (Figs. 3(h) and 3(i)). In contrast, in the compound with a linear structure, the central bond collapsed, and isomerization occurred, and the target diyne with two triple bonds was generated (Figs. 3(k) and 3(l)). When DFT calculations were performed, it was found that these sequential reactions are endergonic reactions caused by injecting energy (tunneling current) from the outside. It was also found that the reaction barrier is significantly reduced by temporarily charging the molecule so that it is monovalent or divalent with electrons from the probe. That is, in order to isomerize flat molecules with a probe, a NaCl thin film, which is a reaction field, is important.

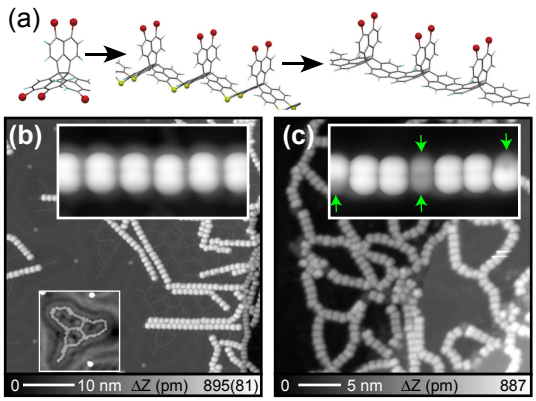

Fig. 4. (a) Precursor molecule, the intermediate, and product of the three-dimensional graphene nanoribbon (3D-GNR). (b) 3D-organometallic compound (OMC) and (c) GNR.

3.2 Addition reaction by probe

Next, we will introduce an addition reaction, in which atoms and molecules are joined by a probe [22]. In this study, a three-dimensional GNR was synthesized, and "local probe chemistry" was performed to manipulate the C–Br bond protruding from the substrate with a probe. So far, GNRs with various width and edge states, and even different introduced elements have been synthesized [19]. However, all GNRs synthesized so far have a flat shape. Therefore, in order to extend this to three dimensions, a propellane molecule with a three-dimensional structure was used as precursor (Fig. 4(a)). By vapor deposition onto Au(111) and Ag(111) and further heating, we succeeded in synthesizing a three-dimensional organometallic compound (OMC) and GNR (Figs. 4(b) and 4(c)). Two bromine atoms, both protruding vertically from each unit, were observed. In addition, in 3D-GNR generated by heating to a high temperature of

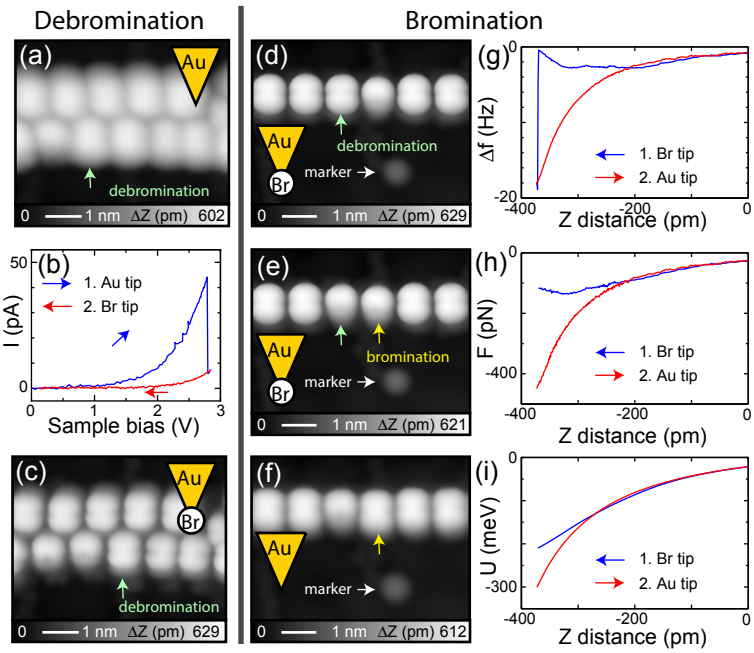

Fig. 5. (a) STM topography taken before the debromination. (b) *I*–*V* curve taken during the debromination. (c) STM topography after the debromination. (d–f) Bromination reaction by the local probe. (g) Frequency shift curve measured during the addition reaction, (h) the extracted force and (j) potential curves.

400 °C, some C–Br bonds collapsed due to heat were observed.

An addition reaction using this three-dimensional carbon nanostructure is described. First, an Au probe was positioned on the bromine atom, and a bias voltage was swept while measuring the tunneling current (Fig. 5(a)). The current decreased at a voltage of 2.6 V (Fig. 5(b)). Subsequently, when STM imaging was performed, the bromine atom directly under the probe was desorbed and became a radical unit (Fig. 5(c)). Moreover, as the obtained contrast became clearer, it was found that the probe was terminated by the removed bromine atom. This elimination reaction is extremely reproducible, and it is possible to sequentially remove bromine from a targeted site. It was also found that the voltage necessary for causing the elimination reaction is almost constant. From the DFT calculations, it was found that an excitation of the π^* orbital of the molecule cleaves the C–Br bond. Furthermore, it was also found that in this three-dimensional structure, the six-membered ring from which bromine was desorbed was separated from the metal substrate, so that radicals can be maintained even without a NaCl thin film.

Next, an addition reaction using a bromine probe is described. First, an Au probe was brought into contact to adsorb a single atom of gold, which is a marker, onto the Au(111) surface (Fig. 5(d)). Subsequently, two bromine atoms were removed by an elimination reaction. Using this process, a probe terminated with a bromine atom was obtained (Fig. 5(e)). Next, while detecting the resonance frequency, which is the signal of AFM, the Br probe was gradually brought closer to the target radical in the vertical direction. A sudden change was detected at $Z = -380$ pm (Fig. 5(g)). Subsequently, when 3D-OMC was observed, it was found that the bromine atom had bonded (Fig. 5(f)). In addition, as the bromine atom at the tip of the probe had moved, it changed the contrast of the STM topographic

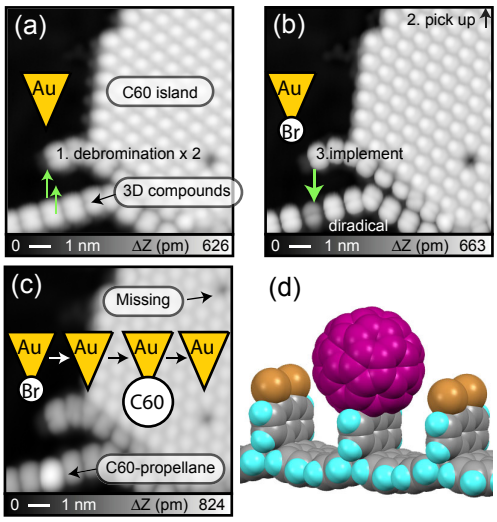

Fig. 6. (a) STM topography of the 3D-OMCs and fullerene molecules. (b) Synthesis of the diradical species and (c) the complex of 3D-OMC and fullerene. (d) Schematic drawing of the product.

image obtained with the Au probe. By integrating the measured frequency shift, the force and potential could be obtained. It was found that just before the addition reaction, the probe was already approaching the region in which the repulsive force is stronger than the maximum value of the attractive force (Fig. 5(h)). Furthermore, it was found that the potential of about 100 meV changes before and after the addition reaction (Fig. 5(i)).

Finally, there was a union with a fullerene molecule, which resulted in a different molecule. After surface synthesis of 3D-OMC, a fullerene molecule was adsorbed onto a surface (Fig. 6(a)). As this structure is larger than a bromine atom, both bromine atoms in the unit were removed (Fig. 6(b)). For the process, the probe was terminated with a bromine atom. As the fullerene molecule could not be picked up as it was, it

was once removed from Au (111) and then returned to the Au probe. Subsequently, we succeeded in synthesizing a complex with a fullerene molecule and 3D-OMC by picking up the fullerene molecule in the part indicated by the arrow and bringing it closer to the radical obtained by the earlier elimination reaction (Figs. 6(c) and 6(d)). This bond is considered to be due to the [2+2] addition reaction. In this way, by making full use of "local probe chemistry", we realized the introduction of different atoms and molecules to the intended molecular site.

4. Conclusion

We think it is no exaggeration to say that the "local probe chemistry" introduced in this paper, which is capable of manipulating structures at the single-molecule level, is a new research area that has been pioneered along with the development of scanning probe microscopy. In the future, developments such as the synthesis of various novel compounds and their functional development, and further, the manufacture of novel devices using these can be expected.

Acknowledgments

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Technical terms

Graphene nanoribbon
A one-atom layer carbon material with the width of a nanometer. It is attracting attention as a next-generation device element because can have a variety of electrical characteristics depending on its width and edge structure.

Organometallic compound
General term for a compound with a bond between a carbon and a metal. The term metal includes alkali metals, alkaline earth metals, transition metals, main group elements, and further, it also includes metalloids, such as silicon.

[2+2] Addition reaction
A cycloaddition reaction in which two different Π electron systems form a four-membered ring and fuse. It also occurs when fullerene molecules dimerize.

Sondheimer–Wong diyne
A molecule organically synthesized by Wong, Garratt, and Sondheimer et al. in 1976.

Profile

Shigeki Kawai received his doctor degree in Engineering from the University of Tokyo in 2005. After he worked as a postdoc in EMPA, Switzerland and a senior researcher in University of Basel, Switzerland, he became a principal researcher in National Institute for Materials Science in 2016. In 2020, he became a group leader as well as an associate professor in University of Tsukuba.