

Molecular Nanotechnology Research Section

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1. Introduction

Nanotechnology is essential for highly efficient energy use. Our group studies the basics of assembling small molecules into the advanced materials and devices in energy sector with high efficiency. We have already developed several unique techniques which are totally new molecular assembling methodology such as 'electro-chemical Epitaxial Polymerization' and 'Two-Zone Chemical Vapor Deposition (2Z-CVD)' which enable to produce molecular wires on metal surface from small molecules. By using these techniques, organic electronic devices such as field-effect transistors and organic solar cells will be developed.

Main research achievements in Molecular Nanotechnology Research Section in 2021 are described below.

2. Bottom-Up On-Surface Synthesis of Edge-functionalized Graphene Nanoribbon

Graphene nanoribbons (GNRs) have shown great potential for electronics, optoelectronics, and photonics. These properties strongly depend on width and edge structure of them. Therefore, precisely controlled width and edge structure are required for desired properties. Bottom-up synthesis of GNRs is a one of suitable method to satisfy these requirements because of definition of their edge structures and widths by the shape of precursors. Atomically precise synthesis of armchair-edged GNRs have already been achieved under ultra-high vacuum (UHV) condition. However, given GNRs in this method were low yield and density was still low. Therefore, it was difficult to develop organic electronic devices with them. To develop devices, high-yield fabrication of assembled GNR films, isolation, and device fabrication are required.

We have developed 2Z-CVD to produce densely packed, parallelly aligned self-assembled GNRs on Au(111) under low vacuum condition of 1 Torr from halogenated polycyclic aromatic hydrocarbon (PAH) precursors. This technique successfully produced a series of armchair-edged GNRs in high yield. Attractive features of this method originate from an independent temperature-control of radical-generation process

(zone 1) and the growth process (zone 2), which afforded GNRs in high yield without using UHV conditions. The precursor was sublimated to the Au(111) substrate in zone 2 by passing through zone 1 in a quartz tube. The mechanism is supposed to involve radical generation in zone 1, polymerization of the radicals on the Au(111) substrate in zone 2, and subsequent dehydrogenation to form GNRs.¹ Additionally, we demonstrate a new concept of 'conformation-controlled surface catalysis'; the 2Z-CVD of the 'Z-bar-linkage' precursor, which represents two terphenyl units are linked like a 'Z', exhibiting flexible geometry that allows it to adopt chiral conformations with height-asymmetry on a Au(111) surface, results in the efficient formation of acene-type GNRs with a width of 1.45 nm through optimized cascade reactions. These cascade reactions on surface include the production of self-assembled homochiral polymers in a chain with a planar conformation, followed by efficient stepwise dehydrogenation via a conformation-controlled mechanism. Our proposed concept analogous to the biological catalyst, enzyme, is useful for the fabrication of new nanocarbon materials.²

Recently, GNRs having asymmetrically functional substitution at each edge have attracted much attention due to realization of ferroelectric or ferromagnetic property predicted by theory. However, it has been difficult to produce them because of decomposition of functional substitution at high temperature process during dehydrogenation reaction. To overcome the problem, we have developed low temperature GNR growth method with hydrogen acceptor.

After producing precursor polymers using 2Z-CVD method with Z-bar-linkage having different substitution at each edge as precursor, hydrogen acceptor was fed into the reactor (evacuated quartz tube), which promote dehydrogenation reaction resulting in giving asymmetrical GNRs without decomposition of functional substitution at lower temperature. Then, we have succeeded in direct observation of asymmetrical GNRs produced on Au(111) with low-temperature scanning tunneling microscope.

3. Solution Synthesis of Asymmetrically Function-

alized Graphene Nanoribbon toward the Application for Functional Materials

Solution-phase synthesis is one of the most promising strategies to obtain well-defined graphene nanoribbon (GNR) with tunable electronic and optical properties. Asymmetrically edge-functionalized GNR have attracted a great deal of interest in view of the relationship between the unique structure and properties. Several theoretical predictions have been made to change the properties of these systems through edge modifications. Introduction of different functional groups to the edges of GNR backbone would offer a promising strategy to exhibit new properties. Although the solution-phase syntheses of GNRs having symmetric substitutions have already reported, our approach, however, has remained unexplored.

We previously reported the on-surface synthesis of acene-type GNR from the Z-shaped precursor which consists of two terphenyl units. Inspired by this work, we envisioned that the asymmetrically substituted GNRs would be obtained from asymmetrically Z-shaped precursor in the solution synthesis. However, the desired product was not obtained probably due to the skeletal rearrangement in the oxidative dehydrogenation reaction. To develop the synthetic method for asymmetrically edge-functionalized GNR, we have synthesized nanographenes as a model compound and GNRs from Z-shaped precursor by Pd-catalyzed cyclization followed by oxidative dehydrogenation reactions.

Based on this method, we investigated the synthesis of GNR having symmetric substitutions. As a result, we have developed the synthetic method via head-to-tail polymerization followed by cyclization with Pd-catalyzed bond formations and oxidative dehydrogenation reactions. This method is applicable to the preparation of asymmetric GNR having different functional groups at opposite side of the edges. We developed this method for the asymmetric GNR. The relationship between the functionalization of edge structures and their properties was identified by absorption spectra.

As an additional step, we designed asymmetric functional GNR. Asymmetrically functionalized and sterically hindered GNRs adopt twisted conformation and have dipolar moment along long axis by asymmetrically modifying both edges. We hypothesized that the orientation of the twisted direction would be controlled by applying an electric field. We succeeded in the preparation of helically twisted GNR with modified synthetic methods. As a result, when the positive and negative electric fields were applied to asymmetrically-functionalized GNR-doped liquid crystal, inversions of the CD signal were observed. These results indicated that the helical switching take place by applying electric field.

5. Manifold dynamic non-covalent interactions for

steering molecular assembly and cyclization

Non-covalent interactions that govern many chemical and biological processes is crucial for the design of supramolecular and controlling molecular assemblies and their chemical transformations. However, the characterization of weak interactions in complex molecular architectures at the single bond level has been a longstanding challenge.

We employed bond-resolved scanning probe microscopy combined with an exhaustive structural search algorithm and quantum chemistry calculations to elucidate multiple non-covalent interactions that control the cohesive molecular clustering of well-designed precursor molecules and their chemical reactions. The presence of two flexible bromo-triphenyl moieties in the precursor leads to the assembly of distinct non-planar dimer and trimer clusters by manifold non-covalent interactions, including hydrogen bonding, halogen bonding, C-H $\cdots\pi$ and lone pair $\cdots\pi$ interactions. The dynamic nature of these weak interactions allows for transformation of the arrangement of monomers in the assembled clusters as molecular density increases, which alters the reaction pathways in the subsequent on-surface synthesis of cyclized products. Our findings highlight a vital route for controlling on-surface supramolecular assemblies and steering their chemical transformations through manipulation of manifold dynamic non-covalent interactions.³

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