

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 2020 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

On the other hand, fully π -conjugated 2D structure attract much attention since they can provide conducting carbon-based nanostructures with holey structure suitable for various electronic applications. Utilization of large fully π -conjugated building blocks such as GNRs, which are 1D carbon-based nanowires, is becoming a promising approach to produce extended 2D π -conjugated systems via surface assisted lateral fusion of GNR chains.

However, it was difficult to efficiently create such sophisticated GNR-linkage structures, since their formation is based on a stochastic surface reaction that requires closed proximity between the precursors on the surface.

We have already successfully produced carbon-based 2D materials, named 2D-Graphene Nanoribbon Networks (GNNs) via lateral fusion of well-organized acene-type GNRs.

Acene- and armchair-type 2D-GNNs were fabricated on the surface of Au(111) through the thermally induced interchain reactions of densely

packed self-assembled GNRs (5-CGNR-1-1 and 7-AGNR), which is the new concept of transforming 1D chains into a 2D network.

The thermal conductivity of 2D-GNNs generated from 5-CGNR-1-1 shows a value of $0.11 \text{ W m}^{-1} \text{ K}^{-1}$, which is one of the lowest values among carbon-based materials as well as inorganic semiconductor materials, while maintaining the electrical conductivity of 188 S m^{-1} . These findings will open new perspectives in the field of research on the utilization of GNRs for TE applications.³

Additionally, introduction of functional group into GNR is of interest because of creating electronical asymmetry. However, it was difficult with on-surface synthesis because of decomposition of functional group at high temperature during dehydrogenation reaction to form GNR from precursor polymer. Now we focused on this great challenge with new concept.

3. Solution Synthesis of Asymmetrically Functionalized 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 from Z-shaped precursor by Pd-catalyzed cyclization followed by oxidative dehydrogenation reactions. The spectroscopic and

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. The relationship between the functionalization of edge structures and their properties will be explored.

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