

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 2023 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 is required for desired properties. Bottom-up synthesis of GNRs is one of the suitable methods to satisfy these requirements because of the definition of their edge structures and widths by the shape of precursors. Atomically precise synthesis of armchair-edged GNRs has 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. The attractive features of this method originate from an independent temperature control of the 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 an 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 the 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 an asymmetrically functional substitution at each edge have attracted much attention due to the realization of ferroelectric or ferromagnetic properties predicted by theory. However, it has been difficult to produce them because of the decomposition of functional substitution at high-temperature process during the dehydrogenation reaction. To overcome these drawbacks, we have developed a brand new method, molecular-vapor-assisted low-temperature growth (MVLTG), based on a massive dose of gaseous hydrogen-accepting molecules to the prepolymer on the metal surface at a low temperature.

After producing precursor polymers using the 2Z-CVD method with Z-bar-linkage having a different substitution at each edge as a 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 a lower temperature. Then, we succeeded in the direct observation of asymmetric GNRs produced on Au(111) with a low-temperature scanning tunneling microscope. The low-voltage STM measurement and dI/dV mapping suggest that

MVLTG successfully enhanced the dehydrogenation reaction without the decomposition of the functionalized group of the GNRs' edges.³⁻⁵

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 nanoribbons (GNRs) with tunable electronic and optical properties. Asymmetrically edge-functionalized GNRs have attracted a great deal of interest in view of the relationship between their unique structure and properties. Several theoretical predictions have been made to change the properties of these systems through edge modifications. The introduction of different functional groups to the edges of GNRs backbone would offer a promising strategy to exhibit new properties. Although the solution-phase syntheses of GNRs having symmetric substitutions have already been 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-tale 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 sides 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 moments along the long and short axis by asymmetrically modifying both edges. We hypothesized that polarity of the twisted GNR would be controlled by applying an electric field. We succeeded in the preparation of helically twisted GNR through modified synthetic methods and tested voltage-current characteristics in the solid state with sandwich-type

cell. As a result, when the positive and negative voltage were swept up to 30 V, clear peaks probably due to ferroelectric properties were observed. These results indicated that conformational changes of twisting molecules took place even in the solid state by applying voltages.

4. Deceptive orbital confinement at edges and pores of carbon-based 1D and 2D nanoarchitectures

The properties of graphene-based nanomaterials are defined by their electronic structure. However, when conducting experiments using scanning tunneling microscopy/spectroscopy (STM/STS) on graphene nanoribbons (GNRs), nanographenes, and nanoporous graphene (NPG), researchers have often observed an apparent confinement of electronic orbitals into the edges and nanopores. This has led to dubious interpretations such as image potential states or super-atom molecular orbitals. Our research shows that these measurements are subject to a wave function decay into the vacuum, which masks the undisturbed electronic orbital shape. To explore this, we used Au(111)-supported semiconducting gulf-type GNRs and NPGs as model systems fostering frontier orbitals that appear confined along the edges and nanopores in STS measurements. DFT calculations confirm that these states originate from valence and conduction bands. The misleading electronic orbital confinement observed is caused by a loss of Fourier components, corresponding to states of high momentum. This effect can be generalized to other 1D and 2D carbon-based nanoarchitectures and is important for their use in catalysis and sensing applications.⁶

References

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3. *Adv. Mater. interface*, **2023**, 10, 2300214.
4. *J. Phys. Chem. C*, **2023**, 127(22), 10541-10549.
5. *Chem. Plus Chem.*, **2024**, <https://doi.org/10.1002/cplu.202300775>
6. *Nat. Commun.*, **2024**, 15, 1062.

Collaboration Works

坂口浩司, 小島崇寛, 信末俊平, ミュンヘン工科大学 (ドイツ), CO₂ 選択的吸着に向けた GNR ナノボア材料の開発

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Grant-in-Aid for Scientific Research

坂口浩司, 基盤研究(B), 電子的非対称型グラフェンナノリボンの表面合成技術の開発と応用

坂口浩司, 挑戦的研究 (萌芽), 分子スケール極細幅を持つ黒リン・ナノリボンのボトムアップ合成技術の開発

小島崇寛, 基盤研究(C), 巨大強誘電性を志向した非対称エッジ型 GNR の低温表面合成

信末俊平, 基盤研究(C), グラフェンナノリボンの構造的特徴を活かした有機強誘電体の開発

2. Others

坂口浩司, (株)KRI, ナノ構造炭素材料の構造解析.

Publications

T. Kojima, C. Xie, K. Patel, S. Nobusue, K. Fukami, H. Sakaguchi, Molecular-Vapor-Assisted Low-Temperature Growth of Graphene Nanoribbons, *Journal of Physical Chemistry C*, 127, 22, 10541-10549, 2023

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I. Piquero-Zulaica, E. Corral-Rascón, X. Diaz de Cerio, A. Riss, B. Yang, A. Garcia-Lekue, M. A. Kher-Elden, Z. M. Abd El-Fattah, S. Nobusue, T. Kojima, K. Seufert, H. Sakaguchi, W. Auwärter, J. V. Barth, Deceptive orbital confinement at edges and pores of carbon-based 1D and 2D nanoarchitectures, *Nature Communications*, 15, 1062, 2024

T. Kojima, C. Xie, H. Sakaguchi, On-Surface Fabrication toward Polar 2D Macromolecular Crystals, *ChemPlusChem*, 2024

Presentations

T. Kojima, Low-temperature growth of functionalized GNR with electrochemical on-surface synthesis, The 14th International Symposium of Advanced Energy Science, 京都大学宇治キャンパス, 2023.9.1