

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 advanced materials and devices in the energy sector with high efficiency. We have already developed several unique techniques, which are totally new molecular assembling methodologies, such as ‘Two-Zone Chemical Vapor Deposition (2Z-CVD)’, ‘Electrochemical on-surface synthesis’, which enable the production of graphene nanoribbons (GNRs) on metal surfaces from small molecules. Additionally, the photo-assisted bottom-up technique enables the synthesis of orange phosphorus, which is a newly developed allotrope of phosphorus. By using these techniques, organic electronic devices such as field-effect transistors and organic solar cells, as well as energy-conversion materials, will be developed.

The main research achievements in Molecular Nanotechnology Research Section in 2025 are described below.

2. Formation Mechanism of Orange Phosphorus via Photoassisted Bottom-Up Synthesis

We studied the formation mechanism of orange phosphorus, a one-dimensional polar phosphorus allotrope composed of repeating linear $[P_8]P_2[$ units, synthesized by a photoassisted bottom-up approach from solution-processable Na_2P_{16} precursor films. Orange phosphorus is structurally distinct from previously known red phosphorus allotropes and shows excellent piezoresistive properties. In the present work, we focused on clarifying how the precursor is transformed into this unusual polar chain structure under laser irradiation.

Experimental Raman analysis revealed that the reaction proceeds stepwise from amorphous Na_2P_{16} to crystalline Na_2P_{16} , then to NaP_{15} , and finally to orange phosphorus. Structural characterization by HAADF-STEM and SAED confirmed the formation of the one-dimensional pentagonal tubular chain structure of orange phosphorus. In addition, controlled experiments demonstrated that trace oxygen plays a decisive role in the conversion of NaP_{15} to orange phosphorus, whereas excessive oxygen leads to decomposition or

shifts the reaction pathway toward type-II red phosphorus.

To understand this process theoretically, DFT calculations were performed on plausible coupling and rearrangement pathways. The calculations suggested that polymerization proceeds through heterocoupling between Na_2P_{16} and its photo-fragmented intermediate, followed by chain elongation to form NaP_{15} -related species. Subsequent oxidation selectively removes ionic linkage sites and promotes rearrangement into the isolated linear $[P_8]P_2[$ chain. These findings clarified how photochemical, photothermal, and oxidative processes cooperate in the formation of orange phosphorus, providing a mechanistic basis for the controlled creation of polar phosphorus allotropes.

3. Oxygen-Doped Graphene Nanoribbons with High Catalytic Performance in Chemical Etching of Silicon

We investigated the catalytic performance of oxygen-doped graphene nanoribbons (5A-OGNRs) in vapor-phase chemical etching of silicon. Metal-assisted chemical etching is widely used for silicon nanostructuring, but residual metal contamination remains a serious drawback for device applications. To address this issue, we explored carbon-based nanoribbons as alternative catalysts and found that oxygen-doped 5-armchair graphene nanoribbons exhibit remarkably high catalytic activity. In vapor-phase etching experiments, 5A-OGNRs showed a significantly higher etching rate than undoped 5A-GNRs and 7A-GNRs, demonstrating the strong effect of edge functionalization and ribbon structure on catalytic performance.

To clarify the origin of this enhanced activity, we analyzed the hydrogen peroxide reduction process, which governs the etching reaction under the present vapor-phase conditions. DFT calculations showed that oxygen doping induces localized high charge-density active sites on carbon atoms adjacent to the doped oxygen atoms. These sites enhance H_2O_2 adsorption and make the reduction process more favorable. The calculated adsorption energy of H_2O_2 on 5A-OGNR was lower than that on undoped GNRs, supporting stronger reactant binding at the active sites. In addition, transition-state analysis revealed that the activation

barriers for key elementary steps are lower in 5A-OGNR than in the comparison systems, thereby explaining its superior catalytic performance.

The study demonstrated that the high catalytic activity of 5A-OGNR originates not simply from the carbon framework itself, but from oxygen-induced electronic structure modulation that promotes both adsorption and reaction kinetics. These results establish oxygen-doped graphene nanoribbons as promising low-contamination alternatives to noble-metal catalysts for silicon etching and provide a molecular-level design principle for future carbon-based catalytic materials.

4. Helical Molecular Cages with sp-Conjugated Linkages

We synthesized a conjugated helical molecular cage composed of two 1,3,5-tris(phenylethynyl)benzene units connected by three diyne linkers. This work was motivated by the idea that rigid π -conjugated linkers can impose geometric constraints, thereby generating helically twisted three-dimensional molecular architectures. The cage was successfully constructed via irreversible carbon-carbon bond formation via Glaser-type coupling, providing an efficient route to a topologically complex conjugated framework.

Single-crystal X-ray crystallographic analysis revealed that the product adopts a helical molecular structure with large twist angles and exists in the crystal as a 1:1 mixture of *P*- and *M*-enantiomers. Although diyne units are often regarded as relatively rigid, the present cage showed unexpectedly dynamic conformational behavior. Variable-temperature NMR measurements indicated that racemization between the two enantiomeric conformations occurs rapidly on the NMR timescale. This result suggests that the diyne-linked framework exhibits greater conformational flexibility than might be expected from its formally linear, sp-conjugated structure.

This study provides a new example of a helical conjugated cage with dynamic chiral behavior and highlights the importance of linker flexibility in controlling three-dimensional molecular shape and stereodynamic properties. The results also suggest that sp-conjugated cage architectures can serve as useful platforms for designing chiral functional spaces and responsive molecular systems based on reversible conformational interconversion.

5. Aryl Shift Rearrangement in Scholl-Type Reaction Toward Nanographene

We investigated the reaction mechanism of oxidative cyclodehydrogenation toward nanographene synthesis through a Scholl-type reaction. In this study, an unexpectedly rearranged nanographene product was obtained instead of the initially designed fused framework. Structural analysis revealed that the product was formed via sequential 1,4- and 1,2-aryl shift rear-

rangements during dehydrogenative cyclization. Single-crystal X-ray crystallographic analysis was crucial for determining the final molecular structure because conventional spectroscopic analysis alone was insufficient to unambiguously assign the rearranged framework.

To clarify the origin of this unusual transformation, mechanistic studies were conducted by combining intermediate analysis with density functional theory (DFT) calculations. Mass spectrometric analysis of the intermediate products suggested that partially cyclized species were formed first, and these intermediates subsequently underwent skeletal rearrangements to produce the final nanographene structure. DFT calculations indicated that both arenium cation and radical cation mechanisms can operate in the rearrangement process, and that the preferred pathway depends on the size and position of the migrating aryl groups. In particular, larger biphenyl- or triphenylenyl-type units tend to undergo arenium cation pathways, whereas smaller monophenyl groups favor radical cation pathways. These results provide important mechanistic insight into rearrangement reactions in Scholl chemistry and offer a new design principle for synthesizing otherwise difficult nanographene frameworks.

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2. Others

(非開示)

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Presentations

(該当なし)