Vectorial On-Surface Synthesis of Polar 2D Graphene Nanoribbon Crystals

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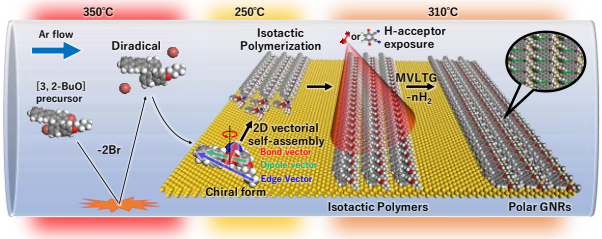
The asymmetric introduction of functional groups into graphene nanoribbons (GNRs) is promising due to its potential to provide novel electronic and magnetic properties as theoretically predicted. Though traditional on-surface bottom-up synthesis has succeeded in creating various types of GNRs, it struggles to realize this concept due to the difficulty of stereoregular polymerization, degradation of the thermally sensitive functional groups during prepolymer dehydrogenation and the tendency for overall polarity cancellation during agglomeration.[1]

In this study, we designed a ‘compass’ precursor possessing three independent vectors: a vector for bonding, an edge vector for inducing intermolecular forces in one direction, and a dipole vector for electronic asymmetry by asymmetrically introducing a butoxy functional group to Z-type polyphenylene precursors. Our developed ‘two-zone chemical vapor deposition’ enabled isotactic polymerization of these precursors under 250°C via the vectorial self-assembly of chiral precursor diradicals.[2] The isotactic prepolymers were then successfully converted into polar GNRs via newly developed ‘molecular-vapor assisted low temperature growth (MVLTG)’ technique (exposed to oxygen at a pressure of 0.8 kPa for 5 min at 310°C), which was capable of promoting the dehydrogenation reactions by exposure to hydrogen-accepting molecular vapor successfully forming polar 2D crystalline structures.[3] Additionally, we recently demonstrated Janus GNR, which has an asymmetric edge structure, zigzag and coved edge, resulting in ferromagnetic with the asymmetric Z-type precursor.[4]



1) T. Kojima, C. Xie, H. Sakaguchi, *ChemPlusChem* **2024**, 89, e202300775. 2) T. Kojima, K. Patel, S. Nobusue, A. Mahmoud, C. Xie, T. Nakae, S. Kawai, K. Fukami, H. Sakaguchi, *Adv. Mater. Interfaces* **2023**, 10, 2300214. 3) T. Kojima, C. Xie, K. Patel, S. Nobusue, K. Fukami, H. Sakaguchi, *J. Phys. Chem. C* **2023**, 127, 10541. 4) S. Song, Y. Teng, W. Tang, Z. Xu, Y. He, J. Ruan, T. Kojima, W. Hu, F. J. Giessibl, H. Sakaguchi, S. G. Louie, J. Lu, *Nature*, **2025**, DOI: https://doi.org/10.1038/s41586-024-08296-x.