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報告番号	※　甲　第　　号

主　論　文　の　要　旨

論 文 題 目　Structure-Controlled Synthesis and Characterization of Carbon Nanotubes and Graphene Nanoribbons
（カーボンナノチューブとグラフェンナノリボンの構造制御合成と評価）

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論　文　内　容　の　要　旨

Carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) are unique carbon nanostructures with interesting structural and electronic properties. In addition to their exceptional mechanical flexibility, they exhibit versatile band gap features that strongly depend on size. Changes in tube diameter or ribbon width result in significantly different electronic states of metals or semiconductors. They have been anticipated to play an essential role in future nano- and optoelectronic devices. Understanding and controlling their synthesis is of utmost importance to exploit their electronic and optical properties in technological applications as well as to satisfy fundamental scientific interests. In this thesis, the fabrication of these sophisticated materials was investigated using the so-called nano-test tube chemistry.

Chapter 1 introduces CNTs and GNRs through a discussion of their structural features, electronic properties, and fabrication methods. In addition, it reviews reactions performed in the inner space and on the outer sidewall of the CNTs, which represent the two core experimental methods used in this study. Chapter 2 describes the commonly used techniques involved in the characterization of these nanostructures. Emphasis is placed on high-resolution transmission electron microscopy imaging (HRTEM) and optical measurements (Raman and optical

absorption spectroscopy), which are indispensable to qualitative and quantitative analyses.

Chapter 3 presents the selective synthesis of CNTs *via* the twisting of GNRs. An approach to achieve predetermined growth was developed by performing reactions in the inner space of the CNT templates. The possibility of converting GNRs into CNTs was explored by using different molecular precursors. Such a transformation was accomplished by heating perylene-3,4,9,10-tetracarboxylic dianhydride at 1200 °C. (7, 2) and (8, 1) CNTs formed preferentially as a result of the thermally induced self-entanglement of one or two perylene ribbons. The process involved was confirmed by using an aberration corrected-HRTEM imaging along with quantum chemical molecular dynamic simulations. Since the reaction is solely governed by the template tube diameter and the structural design of the molecular precursor, achieving a right combination of these parameters is the key to the success of this synthetic route.

Chapter 4 addresses the optical properties of ultrathin GNRs confined in CNTs. The GNRs were fabricated using coronene precursors, which underwent extensive polymerization to give long well-defined structures with a moderate heating at 700 °C. The optical absorption spectra of these extended coronene-derived ribbons are studied through diazonium sidewall functionalization, by which the optical contributions of the template CNTs are eliminated. The extended π-conjugation is characterized by the shifts of the optical absorption bands toward lower energies. The E_{11} and E_{22} peaks corresponding to the optical transitions between the van Hove singularities in the electronic density of states of the obtained ribbons were observed at 1.53 and 3.36 eV, respectively. These values are found to be in good qualitative agreement with the first-principles calculations.

Finally, chapter 5 concludes the thesis with a summary and discussion on future perspectives. Novel synthetic and characterization means are illustrated in this study, complementing present available techniques. The study enlightens on not only the fabrication of future nanomaterials, but also the understanding of quasi-one dimensional physics and chemistry as a whole.