Title: Structure-Controlled Synthesis and Characterization of Carbon Nanotubes and Graphene Nanoribbons

Abstract

Carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) are unique carbon nanostructures with interesting 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 substantially different electronic states of metals or semiconductors. For that, 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 and to satisfy fundamental scientific interests.

This thesis consists of five chapters. The first two chapters aim to familiarize readers with the subjects studied. They provide a fundamental background to aid the understanding of concepts discussed in the following chapters. It proceeds next to the main topics studied, where the fabrication of these sophisticated materials, i.e. the CNTs and GNRs, was investigated inside the hollow space of large-diameter CNT templates, or the so-called nano-test tube chemistry. The thesis ends with general conclusion remarks on the future perspectives. Detailed description to the experimental procedure involved is available in Appendix A. Related publications are appended as Papers I and II, whereas additional studies conducted but not included in this thesis are enclosed as Papers III to V.

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 practices used in this study. Apart from that, rationale to the studies conducted are stated along with the challenges faced in the relevant field at the end of this chapter to brief the significance of the works carried out. Chapter 2 describes the commonly used techniques involved in the characterization of these nanostructures. Emphasis is placed on high-resolution transmission electron microscopy (HRTEM) imaging and optical measurements (Raman and optical absorption spectroscopy), which are indispensable in qualitative and quantitative analyses. The basic principles of these instrumentations and the related data interpretation can be well understood from this chapter.

Chapter 3 presents the selective synthesis of CNTs via the twisting of GNRs. This peculiar route of fabrication was developed through the fusion reaction performing inside

the CNT templates. The possibility of converting GNRs into CNTs was explored using different molecular precursors of various structures, including picene, pentacene and perylene. 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 with a width of five carbon atoms. The process involved was confirmed by using an aberration corrected-HRTEM imaging along with quantum chemical molecular dynamic simulations. Binding energies calculations conducted on the CNTs to adopt either one or two PTCDA molecules suggest that there are equal chances of getting these two CNT species. It was found that the output chirality is not dictated only by the initial structural geometry of the precursors used, but also by the intermediates formed. Deformed fullerene-like intermediates generally result in the (6, 5) CNTs, while the GNR intermediates give rise to the different tubes based on the ribbons width. A predetermined growth of CNTs with desired structures can be foreseen by tuning the template tube diameter as well as the manipulation of the intermediate ribbon width.

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 at a moderate heating of 700 °C. The optical absorption spectra of these extended coronene-derived ribbons were studied via diazonium sidewall functionalization, by which the optical contributions of the template CNTs were eliminated through disruption of π-conjugation. The extended GNRs fabricated were 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 were found to be in good qualitative agreement with the first-principles calculations. It presents an easy approach to modify the band gap properties of the GNRs synthesized by heat treatment and to unveil the intrinsic properties of such confined materials.

Finally, chapter 5 concludes the thesis with a summary. This study devotes to the novel synthetic and characterization means that complements present available techniques. It sheds much light on not only the fabrication of future nanomaterials, but also the understanding of quasi-one dimensional physics and chemistry as a whole.

Keywords: Synthesis, Carbon nanotubes, Graphene nanoribbons, Optical properties