B-C-N Nanotubes and Related Nanostructures

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Foreword

For many, in the 1980s and early 1990s, the accidental discovery of carbon-based fullerenes and nanotubes heralded the beginning of the nanoscience and nanotechnology revolution. These unique materials promised new chemistries, diverse electronic and thermal properties, extreme mechanical behavior, and novel optical response. Today, a number of applications have been commercially realized and the future, especially for carbon nanotubes, looks bright.

What makes these materials so special? One key feature is the sp^2 chemical bond, the strongest in nature. This hybridized bond is what binds together the carbon atoms in planar graphene and it is even stronger than the tetrahedral sp^3 bonds of diamond. This is the basis for the exceptional strength and stiffness of nanotubes. A second key feature is the relatively light mass of carbon, which, when combined with strong bonds, leads to high vibrational frequencies and transport anomalies such as high thermal conductivity. A third feature is the intrinsic low-dimensional nature of the materials. Carbon nanotubes serve as ballistic, one-dimensional quantum wires.

In the periodic table of the elements, carbon is flanked by boron and nitrogen. As it turns out, boron and nitrogen also form exceptionally strong sp^2 bonds, leading to planar BN configurations. Hexagonal BN, structurally similar to naturally occurring graphite, was synthesized in the early nineteenth century. BN-based planar materials are quite diverse. When combined with carbon, a host of different B–C–N configurations are possible. Many B–C–N-based planar compounds were first synthesized by N. Bartlett at the University of California at Berkeley in the 1970s and 1980s. The discovery of carbon nanotubes led researchers to investigate the possibility of nanotubes formed from other materials. In 1994, M. Cohen, a theorist at Berkeley, predicted that various B–C–N-based nanotubes should be stable, including pure BN nanotubes. Shortly thereafter, BN nanotubes were experimentally realized by A. Zettl, again at Berkeley, in 1995. Hence, the discovery of BN nanotubes was not an accident. Other B–C–N-based nanotubes and nanoparticles (such as nanococoons) have also been synthesized, including those with BC_3 and BC_2N stoichiometry. Generally, B–C–N nanomaterials development has been theoretically guided much more strongly than has carbon nanomaterials development.

B–C–N nanotubes and nanoparticles form an exciting materials set with a phenomenally rich set of physical properties. Pure BN nanotubes are uniformly semiconducting with a large bandgap, independent of diameter, chirality, or wall

number (this is in sharp contrast to carbon nanotubes, where the electronic properties are strongly influenced by geometrical subtleties). However, application of transverse electric fields to BN nanotubes, or mechanical deformation, depresses the local bandgap, opening up the possibility of external voltage-tuned optical components or sensitive transducers. BC_2N nanotubes are predicted to support helical currents. BC_3 nanotubes are predicted to be insulating in isolation but metallic in bundles. Doped BN nanotubes are excellent, stable electron field emission sources. BN nanotubes are useful as hydrogen storage media, with H_2-binding energies significantly larger than those for carbon nanotubes. BN nanotubes have unusual exciton configurations as well as unique spin states, and have exceptional thermal conductivity properties. They can easily be chemically functionalized and are noncytotoxic to living cells; hence, they have important biological applications. B–C–N materials also typically have extreme resistance to chemical degradation and oxidation; BN nanotubes are extremely stable at high temperatures.

Why then, with all the wonderful characteristics of B–C–N nanomaterials, are they relatively unknown compared with pure carbon nanomaterials? One reason is that B–C–N nanotubes and nanoparticles are harder to synthesize than their carbon counterparts. The synthesis temperatures are typically higher, and boron and nitrogen containing precursor materials are more difficult to work with, than those for carbon. Researchers and industrialists today wishing to study or implement B–C–N nanomaterials have limited options for obtaining these materials from commercial vendors. Another reason for the less popular image of B–C–N nanomaterials is that the relevant scientific literature is scattered amongst many different journals, theses, and lectures. In sharp contrast to carbon-based nanomaterials, for which many reference books exist, none such single volume has existed for B–C–N nanomaterials, and reliable information is hard to find.

Hence, this volume on B–C–N nanotubes and nanostructures, superbly edited by Yoke Khin Yap, serves a critical need. It brings together under one cover the full spectrum of B–C–N-based nanomaterial, from theoretical models to synthesis techniques to characterization and application. Chapter authors are leaders in the field, and they have done a magnificent job of distilling the most exciting and most important topics, and presenting them in clear, tractable fashion. This volume represents the first comprehensive book on B–C–N nanomaterials including pure BN, $B_xC_yN_z$, CN, BC, and boron, and will no doubt become a classic reference. The B–C–N field is in its infancy with great science and applications potential; this volume will surely facilitate rapid expansion of the field.

Berkeley, CA Alex Zettl

Preface

The arrangement of carbon atoms differentiates a pencil lead from pricey diamonds. New carbon materials such as fullerenes, carbon nanotubes, and graphene have attracted tremendous research interest and have led to a Nobel Prize. Clearly, the change of bond hybridization and molecular packing among carbon atoms can make very exciting new materials. Materials in the boron nitride (BN) system are structurally similar to the carbon solids. However, carbon and BN materials have different properties. For instance, graphite is a conductor while hexagonal-BN is an insulator. Hybridization of the carbon and BN phases (boron carbon-nitride, BCN or $B_xC_yN_z$) was predicted to create another series of novel materials with tunable properties intermediate to that of their precursors.

Materials within the B–C–N triangular zone offer new vistas for materials research. They include nanostructures of carbon, boron, and compounds constructed of multiple elements using B, C, and N atoms, the smallest atoms that can form the strongest covalent bonds in solids. Clearly, the ability to control bond hybridization, molecular packing, and composition of these materials is important in the creation of new materials. Significant research efforts have been invested in the B–C–N area in the past decade. However, there is no comprehensive reference available for the scientific community. Since this research area has been growing significantly in the past few years, a group of experts have came together in the making of this reference book on B–C–N nanotubes and related nanostructures.

This is the first book emphasizing the latest research on B–C–N nanomaterials, which will complement the many volumes devoted to carbon nanotubes. The contents cover all possible materials within the B–C–N triangular zone: Carbon, BN, BCN, carbon nitrides (CN), boron, boron carbide (B_xC_y), and doped carbon nanostructures. The first chapter provides fundamental background on all B–C–N materials, which is reviewed in detail in subsequent chapters. The chapter by Wang et al. focuses on multiwalled boron nitride nanotubes (BNNTs). This chapter is followed by a review of single wall BNNTs. The chapter by Arenal and Loiseau also summarizes the latest understanding of single wall nanotubes of BN, CN, B_xC_y, and $B_xC_yN_z$. The chapter by Blasé and Chacham outlines theoretical findings on the electronic properties of BNNTs, nanotubes of $B_xC_yN_z$ and novel heterojunctions of CNTs and BNNTs. The chapter by Wirtz and Rubio complements the chapters by Wang et al., Arenal and Loiseau, and Blasé and Chacham by reviewing the phonon

and optical properties of BNNTs. The chapter by Oku focuses on interesting BN nanostructures such as nanocages and nanohorns. The chapter by Yu and Wang describes experimental efforts on interesting nanostructures of CN and $B_xC_yN_z$, which are different from those discussed in the chapter by Arenal and Loiseau. The chapter by Filho and Terrones summarizes efforts on modified CNTs, an emerging area closely associated with CNTs. Finally, the chapter by Lau et al. reviews both experimental and theoretical efforts on boron and boron carbide materials. All these chapters have been carefully planned to fulfill the goal of providing a comprehensive reference book on B–C–N nanomaterials.

The volume editor acknowledges the superior contributions from all participating authors, which has made the successful and timely completion of this book possible.

Houghton, MI Yoke Khin Yap

About the Volume Editor

Professor Yoke Khin Yap received his Ph.D. in 1999 from Osaka University as a "*Monbusho*" scholar. He was a fellow of the *Japan Society for the Promotion of Science (JSPS)* before joining Michigan Tech in 2002. Professor Yap received the National Science Foundation *CAREER* Award in 2005. He has published more than 140 articles including book and encyclopedia chapters, review papers, peer-reviewed articles, and conference proceedings. His research program at Michigan Tech has been supported by the U.S. Department of Army (DOA), National Science Foundation (NSF), Defense Advanced Research Projects Agency (DARPA), the U.S. Department of Energy (DOE), the U.S. Department of Agriculture (USDA), and multiple DOE Nanoscale Science Research Centers. Professor Yap is also the first elected Chair of the user group of the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory.

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