

# Advanced Materials Science and Engineering of Carbon

## 先进碳材料科学与工程

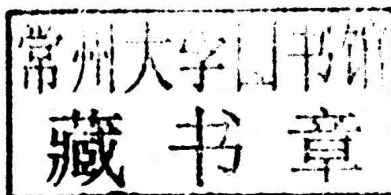
[日] Michio Inagaki [中] Feiyu Kang [日] Masahiro Toyoda [日] Hidetaka Konno

清华大学出版社

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# Preface

Carbon materials, the targeted materials of the present book, are very important in many fields of science, engineering, and technology, and so papers reporting on “carbon material” are published in journals in a wide range of specialties. Even focusing on a specific subject—for example, carbon nanotubes, template carbonization, anode materials for lithium-ion batteries, and so on—huge numbers of scientific papers are published. Therefore, the search of related references published in journals without omission is an onerous and time-consuming task. Naturally, it is not easy to provide a comprehensive overview of a particular subject within the science of carbon and cover the whole range of material released. That is what makes it so challenging; and above all, comprehensive summary and review of the published results are remarkably helpful to many people and vital to further development of the field.

In the present book, the authors attempt to give summaries and reviews on selected themes concerning carbon materials, based on the material and information, as much as is obtainable to us. Principal results in advanced materials science and engineering of carbon materials are reviewed with reference to a vast number of papers published in scientific journals. The book is organized into 17 chapters, including the introduction in Chapter 1. Chapters 2 to 10 are focused on issues of formation and preparation of carbon materials, and Chapters 11 to 17 cover different applications. In Chapters 2 and 3, carbon nanotubes and graphene are reviewed, with emphasis on their formation. Processes with specific procedures and the resultant carbon materials are reviewed in Chapters 4 to 10: they cover carbonization under pressure; graphitization under high pressure, including stress graphitization; glass-like carbons, with special attention to their activation and graphitization; template carbonization to control morphology and pore structure; carbon nanofibers prepared via electrospinning; carbon foams creating new applications; and nanoporous carbon membranes including carbon fiber webs. In Chapters 11 to 17, carbon materials used in specific fields are reviewed: electrochemical capacitors; lithium-ion rechargeable batteries; photocatalysis; spilled-oil recovery; adsorption of hydrogen, methane, volatile organic compounds, and metal ions; highly-oriented and highly-crystalline graphite, emphasizing its high thermal conductivity; and isotropic high-density graphite, emphasizing its nuclear applications.

To understand the advanced science and engineering of carbon materials, a wide range of fundamental knowledge in the field of carbon materials is essential; that is, knowledge of aspects such as carbonization, graphitization, intercalation, and so on, in addition to basic knowledge of chemistry, physics, biology, and other subjects. For readers' convenience, it is recommended to consult *Carbon Materials Science and Engineering: From Fundamentals to Applications*, published by Tsinghua University Press. The book will supply fundamental knowledge on carbon materials and help in the understanding of the broad range of topics in the present book.

It would give great pleasure to the authors if the content of this book can provide useful information which may be used to inspire the readers to new research directions.



# Acknowledgments

The authors would like to express their sincere thanks to the people who kindly provided the data and figures for this book. They also thank all of the people who have taken care of this book in Tsinghua University Press and also in Elsevier.



# Contents

|  |           |
|--|-----------|
| Preface.....   | xi        |
| Acknowledgment .....   | xiii      |
| <b>CHAPTER 1 Introduction.....</b>                               | <b>1</b>  |
| 1.1 Classification of carbon materials .....                     | 2         |
| 1.2 Nanotexture of carbon materials .....                        | 5         |
| 1.3 Microtexture of carbon materials .....                       | 8         |
| 1.4 Specification of carbon materials .....                      | 10        |
| 1.5 Construction of the present book .....                       | 12        |
| References .....   | 12        |
| <b>CHAPTER 2 Carbon Nanotubes: Synthesis and Formation .....</b> | <b>15</b> |
| 2.1 Synthesis of carbon nanotubes .....                          | 16        |
| 2.2 Formation of carbon nanotubes.....                           | 22        |
| 2.2.1 Formation into yarns .....                                 | 22        |
| 2.2.2 Formation into sheets .....                                | 24        |
| 2.2.3 Formation into sponges .....                               | 29        |
| 2.3 Applications of carbon nanotubes .....                       | 30        |
| 2.4 Concluding remarks .....                                     | 35        |
| References .....   | 36        |
| <b>CHAPTER 3 Graphene: Synthesis and Preparation.....</b>        | <b>41</b> |
| 3.1 Preparation through the cleavage of graphite.....            | 42        |
| 3.2 Preparation through the exfoliation of graphite .....        | 45        |
| 3.2.1 Preparation using graphite oxides .....                    | 45        |
| 3.2.2 Preparation using graphite intercalation compounds .....   | 49        |
| 3.3 Synthesis through chemical vapor deposition .....            | 50        |
| 3.4 Synthesis through the organic route .....                    | 56        |
| 3.5 Preparation through other processes .....                    | 57        |
| 3.6 Concluding remarks .....                                     | 59        |
| References .....   | 62        |
| <b>CHAPTER 4 Carbonization Under Pressure .....</b>              | <b>67</b> |
| 4.1 Carbonization under built-up pressure .....                  | 68        |
| 4.1.1 Setup for carbonization under pressure.....                | 68        |
| 4.1.2 Optical texture and carbonization yield .....              | 68        |
| 4.1.3 Particle morphology .....                                  | 70        |
| 4.2 Carbonization under hydrothermal conditions.....             | 74        |



|                  |   |            |
|------------------|---|------------|
| 4.3              | Carbonization under supercritical conditions.....                     | 78         |
| 4.4              | Concluding remarks .....  | 79         |
| 4.4.1            | Temperature and pressure conditions<br>for carbonization .....        | 79         |
| 4.4.2            | Composition of precursors for the formation<br>of carbon spheres..... | 81         |
|                  | References .....  | 84         |
| <b>CHAPTER 5</b> | <b>Stress Graphitization.....</b>                                     | <b>87</b>  |
| 5.1              | Graphitization under pressure .....                                   | 88         |
| 5.1.1            | Structural change in carbons .....                                    | 88         |
| 5.1.2            | Mechanism .....   | 93         |
| 5.2              | Graphitization in coexistence with minerals<br>under pressure .....   | 96         |
| 5.2.1            | Coexistence with calcium compounds .....                              | 96         |
| 5.2.2            | Coexistence with other minerals .....                                 | 99         |
| 5.2.3            | Mechanism for acceleration of graphitization.....                     | 99         |
| 5.3              | Stress graphitization in carbon/carbon composites .....               | 102        |
| 5.3.1            | Acceleration of graphitization.....                                   | 102        |
| 5.3.2            | Mechanism .....   | 105        |
| 5.4              | Concluding remarks .....  | 107        |
| 5.4.1            | Graphitization under pressure .....                                   | 107        |
| 5.4.2            | Occurrence of graphite in nature.....                                 | 108        |
| 5.4.3            | Stress graphitization in carbon/carbon composites .....               | 109        |
|                  | References .....  | 109        |
| <b>CHAPTER 6</b> | <b>Glass-like Carbon: Its Activation<br/>and Graphitization .....</b> | <b>111</b> |
| 6.1              | Activation of glass-like carbon.....                                  | 111        |
| 6.1.1            | Glass-like carbon spheres.....  | 111        |
| 6.1.2            | Activation in a flow of dry air .....                                 | 113        |
| 6.1.3            | Activation in a flow of wet air.....                                  | 117        |
| 6.1.4            | Activation process .....  | 118        |
| 6.1.5            | Direct observation of micropores.....                                 | 121        |
| 6.1.6            | Two-step activation .....   | 123        |
| 6.2              | Graphitization of glass-like carbons.....                             | 124        |
| 6.2.1            | Graphitization through melting .....                                  | 124        |
| 6.2.2            | Graphitization under high pressure .....                              | 126        |
| 6.2.3            | Graphitization in C/C composites .....                                | 128        |
| 6.3              | Concluding remarks .....  | 130        |
|                  | References .....  | 132        |

|                  |   |            |
|------------------|---|------------|
| <b>CHAPTER 7</b> | <b>Template Carbonization: Morphology and Pore Control.....</b> | <b>133</b> |
| 7.1              | Template carbonization for morphological control.....           | 134        |
| 7.1.1            | Inorganic layered compounds .....                               | 134        |
| 7.1.2            | Anodic aluminum oxide films .....                               | 135        |
| 7.1.3            | Organic foams .....   | 138        |
| 7.2              | Template carbonization for pore-structure control.....          | 139        |
| 7.2.1            | Zeolites .....  | 139        |
| 7.2.2            | Mesoporous silicas .....  | 142        |
| 7.2.3            | MgO .....   | 145        |
| 7.2.4            | Block copolymer surfactants (soft templates).....               | 149        |
| 7.2.5            | Metal-organic frameworks .....                                  | 153        |
| 7.2.6            | Other templates .....   | 154        |
| 7.3              | Concluding remarks .....  | 155        |
|                  | References .....  | 159        |
| <b>CHAPTER 8</b> | <b>Carbon Nanofibers Via Electrospinning .....</b>              | <b>165</b> |
| 8.1              | Carbon nanofibers synthesized via electrospinning .....         | 166        |
| 8.1.1            | Polyacrylonitrile.....  | 166        |
| 8.1.2            | Pitch.....  | 170        |
| 8.1.3            | Polyimides.....   | 171        |
| 8.1.4            | Poly(vinylidene fluoride) .....                                 | 171        |
| 8.1.5            | Phenolic resins .....   | 172        |
| 8.2              | Applications .....  | 172        |
| 8.2.1            | Electrode materials for electrochemical capacitors.....         | 172        |
| 8.2.2            | Anode materials for lithium-ion rechargeable batteries....      | 175        |
| 8.2.3            | Catalyst support.....   | 178        |
| 8.2.4            | Composite with carbon nanotubes .....                           | 180        |
| 8.3              | Concluding remarks .....  | 180        |
| 8.3.1            | Carbon precursors .....   | 180        |
| 8.3.2            | Pore-structure control.....                                     | 182        |
| 8.3.3            | Improvement of electrical conductivity .....                    | 184        |
| 8.3.4            | Loading of metallic species.....                                | 185        |
|                  | References .....  | 186        |
| <b>CHAPTER 9</b> | <b>Carbon Foams.....</b>  | <b>189</b> |
| 9.1              | Preparation of carbon foams .....                               | 190        |
| 9.1.1            | Exfoliation and compaction of graphite.....                     | 190        |
| 9.1.2            | Blowing of carbon precursors .....                              | 193        |
| 9.1.3            | Template carbonization .....                                    | 198        |
| 9.2              | Applications of carbon foams .....                              | 201        |

|   |                |
|---|----------------|
| 9.2.1 Thermal energy storage.....   | 202            |
| 9.2.2 Electrodes.....   | 207            |
| 9.2.3 Adsorption.....   | 208            |
| 9.2.4 Other applications .....  | 209            |
| <b>9.3 Concluding remarks .....</b>   | <b>210</b>     |
| References .....  | 212            |
| <br><b>CHAPTER 10 Nanoporous Carbon Membranes<br/>and Webs.....</b>                   | <br><b>215</b> |
| <b>10.1 Synthesis.....</b>  | <b>216</b>     |
| 10.1.1 Pyrolysis and carbonization of organic precursors.....                         | 216            |
| 10.1.2 Templating.....  | 219            |
| 10.1.3 Chemical and physical vapor deposition.....                                    | 222            |
| 10.1.4 Formation of carbon nanotubes and nanofibers .....                             | 223            |
| <b>10.2 Applications .....</b>  | <b>224</b>     |
| 10.2.1 Adsorbents.....  | 224            |
| 10.2.2 Separation membranes .....   | 225            |
| 10.2.3 Chemical sensors and biosensors .....  | 228            |
| 10.2.4 Electrodes .....   | 229            |
| 10.2.5 Other applications.....  | 231            |
| <b>10.3 Concluding remarks .....</b>  | <b>231</b>     |
| References .....  | 233            |
| <br><b>CHAPTER 11 Carbon Materials for Electrochemical<br/>Capacitors.....</b>        | <br><b>237</b> |
| <b>11.1 Symmetrical supercapacitors.....</b>  | <b>239</b>     |
| 11.1.1 Activated carbons .....  | 239            |
| 11.1.2 Templated carbons.....   | 243            |
| 11.1.3 Other carbons .....  | 246            |
| 11.1.4 Carbons containing foreign atoms.....  | 248            |
| 11.1.5 Carbon nanotubes and nanofibers.....   | 252            |
| <b>11.2 Asymmetrical supercapacitors .....</b>  | <b>254</b>     |
| <b>11.3 Asymmetrical capacitors .....</b>   | <b>256</b>     |
| <b>11.4 Carbon-coating of electrode materials .....</b>                               | <b>258</b>     |
| <b>11.5 Concluding remarks .....</b>  | <b>260</b>     |
| References .....  | 261            |
| <br><b>CHAPTER 12 Carbon Materials in Lithium-ion<br/>Rechargeable Batteries.....</b> | <br><b>267</b> |
| <b>12.1 Anode materials.....</b>  | <b>268</b>     |
| 12.1.1 Materials.....   | 268            |
| 12.1.2 Carbon coating of graphite .....   | 270            |

|                   |  |            |
|-------------------|--|------------|
| 12.1.3            | Carbon coating of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .....                | 275        |
| <b>12.2</b>       | Cathode materials .....  | 278        |
| 12.2.1            | Materials.....   | 278        |
| 12.2.2            | Carbon coating of $\text{LiFePO}_4$ .....                                    | 279        |
| <b>12.3</b>       | Concluding remarks .....   | 283        |
|                   | References .....   | 284        |
| <b>CHAPTER 13</b> | <b>Carbon Materials in Photocatalysis.....</b>                               | <b>289</b> |
| <b>13.1</b>       | $\text{TiO}_2$ -loaded activated carbons.....                                | 290        |
| <b>13.2</b>       | Mixture of activated carbon and $\text{TiO}_2$ .....                         | 295        |
| <b>13.3</b>       | Carbon-doped $\text{TiO}_2$ .....  | 297        |
| <b>13.4</b>       | Carbon-coated $\text{TiO}_2$ .....   | 300        |
| <b>13.5</b>       | Synthesis of novel photocatalysts via carbon coating .....                   | 305        |
| 13.5.1            | Carbon-coated $\text{Ti}_n\text{O}_{2n-1}$ .....                             | 305        |
| 13.5.2            | Carbon-coated $\text{W}_{18}\text{O}_{49}$ .....                             | 305        |
| 13.5.3            | $\text{TiO}_2$ co-modified by carbon and iron .....                          | 305        |
| <b>13.6</b>       | Concluding remarks .....   | 306        |
|                   | References .....   | 308        |
| <b>CHAPTER 14</b> | <b>Carbon Materials for Spilled-oil Recovery .....</b>                       | <b>313</b> |
| <b>14.1</b>       | Sorption capacity for heavy oils .....                                       | 314        |
| 14.1.1            | Exfoliated graphite .....  | 314        |
| 14.1.2            | Carbonized fir fibers .....  | 318        |
| 14.1.3            | Carbon fibers .....  | 318        |
| 14.1.4            | Carbon nanotube sponge .....   | 319        |
| 14.1.5            | Other carbon materials .....   | 320        |
| <b>14.2</b>       | Selectivity of sorption .....  | 320        |
| <b>14.3</b>       | Sorption kinetics.....   | 321        |
| <b>14.4</b>       | Cycle performance of carbon sorbents and heavy oils.....                     | 323        |
| <b>14.5</b>       | Preliminary experiments for practical recovery<br>of spilled heavy oils..... | 326        |
| 14.5.1            | Exfoliated graphite packed into a plastic bag.....                           | 326        |
| 14.5.2            | Formed exfoliated graphite.....  | 327        |
| 14.5.3            | Heavy oil sorption from contaminated sand.....                               | 328        |
| 14.5.4            | Sorption of heavy-oil mousse.....  | 329        |
| 14.5.5            | $\text{TiO}_2$ -loaded exfoliated graphite .....                             | 329        |
| <b>14.6</b>       | Concluding remarks .....   | 329        |
| 14.6.1            | Comparison among carbon materials .....                                      | 329        |
| 14.6.2            | Mechanism of heavy oil sorption .....  | 331        |
| 14.6.3            | Comparison with other materials .....  | 332        |
|                   | References .....   | 333        |

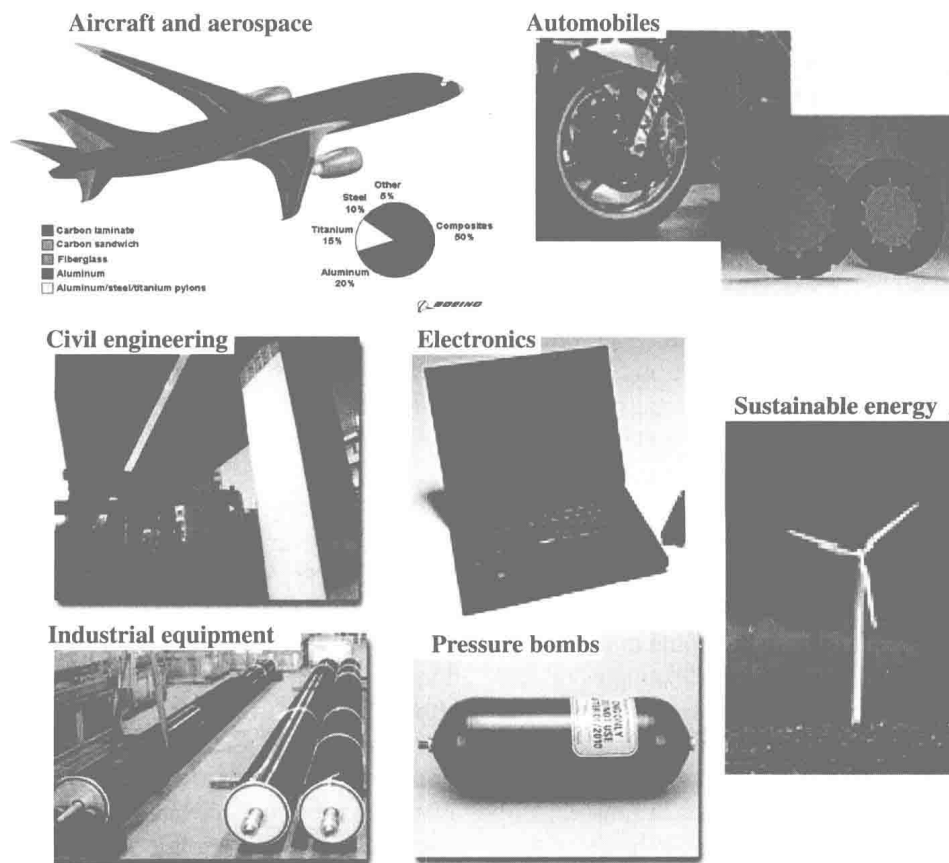
|                   |   |            |
|-------------------|---|------------|
| <b>CHAPTER 15</b> | <b>Carbon Materials for Adsorption of Molecules and Ions.....</b>     | <b>335</b> |
| 15.1              | Adsorption and storage of hydrogen .....                              | 336        |
| 15.2              | Adsorption and storage of methane and methane hydrate .....           | 339        |
| 15.3              | Adsorption and storage of CO <sub>2</sub> .....                       | 343        |
| 15.4              | Adsorption of organic molecules .....                                 | 346        |
| 15.4.1            | Organic gases (including VOCs) .....                                  | 346        |
| 15.4.2            | Organic molecules in water.....                                       | 350        |
| 15.5              | Adsorption and removal of heavy-metal ions in water.....              | 353        |
| 15.6              | Capacitive deionization .....   | 354        |
| 15.7              | Concluding remarks .....  | 356        |
|                   | References .....  | 357        |
| <b>CHAPTER 16</b> | <b>Highly Oriented Graphite with High Thermal Conductivity .....</b>  | <b>363</b> |
| 16.1              | Preparation.....  | 364        |
| 16.2              | Characterization.....   | 366        |
| 16.3              | Carbon materials with high thermal conductivity .....                 | 370        |
| 16.3.1            | Pyrolytic graphite .....  | 370        |
| 16.3.2            | Polyimide-derived graphite .....                                      | 373        |
| 16.3.3            | Natural graphite and its composites .....                             | 374        |
| 16.3.4            | Carbon fibers .....   | 376        |
| 16.3.5            | Carbon nanotubes and graphene.....                                    | 378        |
| 16.3.6            | Diamond and diamond-like carbons.....                                 | 379        |
| 16.4              | Concluding remarks .....  | 382        |
|                   | References .....  | 384        |
| <b>CHAPTER 17</b> | <b>Isotropic High-density Graphite and Nuclear Applications .....</b> | <b>387</b> |
| 17.1              | Production .....  | 388        |
| 17.2              | Properties.....   | 392        |
| 17.3              | Nuclear applications .....  | 400        |
| 17.3.1            | Fission reactors.....   | 400        |
| 17.3.2            | Fusion reactors .....   | 405        |
| 17.4              | Concluding remarks .....  | 406        |
|                   | References .....  | 409        |
| <b>INDEX.....</b> |   | <b>411</b> |

# Introduction

# 1

Carbon materials have always played important roles for human beings; for example, charcoals as a heat source and adsorbent since prehistoric times, flaky natural graphite powder as pencil lead and soot in black ink in the development of communication techniques, graphite electrodes in steel production, carbon blacks for reinforcing tires in the development of motorization, graphite membrane switches making computers and control panels thinner and lighter, carbon fibers for reinforcing plastics, high-purity graphite blocks in nuclear reactors, compounds of graphite with fluorine in lithium primary batteries, graphite in lithium-ion secondary batteries. Many carbon materials have been developed and more will be developed in the future. They are widely used from the home to the industrial setting.

In Figure 1.1, some examples of applications of carbon materials are illustrated, in order to show how widely they are used, although listing every application is not possible here. In the aircraft and aerospace fields, carbon-fiber-reinforced plastics are used in body parts. In automobiles, carbon-fiber-reinforced carbons are used in brakes; carbon/metal composites in brushes; carbon blacks in tires; and activated carbons to create comfortable space in the car, and also in the canister to save gasoline and to avoid air contamination. In the building and civil engineering fields, carbon-fiber-reinforced concrete is successfully used in buildings and bridges exposed to sea water to avoid erosion by salts. Carbon fibers are used for reinforcing the piers of expressways. In electronic devices such as computers and mobile phones, carbon materials are used in power sources as electrodes of primary and secondary batteries, and conductive graphite sheets printed on polymer films are used as switches and conducting leads, helping to make the devices greatly lighter and thinner. To produce semiconductors for electronic devices, like silicon single crystals, carbon/carbon composites for heaters and high-density graphite for crucibles and susceptors are essential. Carbon materials also find their way into sustainable energy development: the blades of windmills consist of carbon-fiber-reinforced composites. To stabilize the varying electricity produced by windmills and solar cells, lithium-ion rechargeable batteries and electrochemical capacitors are essential devices, both using carbon materials as electrodes. Electric conductive carbon rods and carbon blacks support the development of primary batteries. Compounds of graphite with fluorine, graphite fluorides, improve the performance of primary batteries, and the reaction of lithium intercalation/deintercalation into the galleries of graphite is greatly furthering the development of lithium-ion rechargeable batteries. In addition, carbon nanotubes and fullerenes are promoting the development of nanotechnology in various fields of science and engineering.

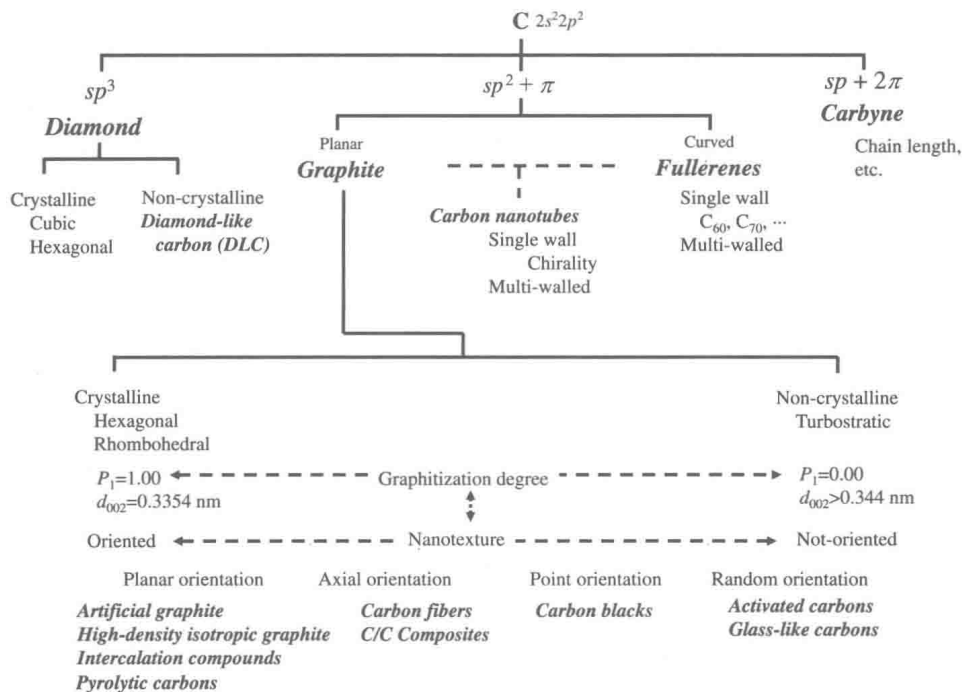


**FIGURE 1.1 Carbon Materials Supporting Our Lives**

Carbon materials are predominantly composed of carbon atoms, only the single element, but they have widely diverse structures and properties. Diamond has a three-dimensional structure, graphite has a two-dimensional nature, while carbon nanotubes are one-dimensional, and buckminsterfullerene,  $C_{60}$ , is zero-dimensional. Fullerenes behave as molecules, although other carbon materials do not. Graphite is an electrical conductor and its conductivity is strongly enhanced by  $AsF_5$  intercalation, becoming almost comparable to that of metallic copper, whereas diamond is completely insulating. Diamond, the hardest material, is used for cutting tools, and graphite is so soft that it can be used as a lubricant.

## 1.1 Classification of carbon materials

Classification of carbon materials has been done on various different bases; for example, the chemical nature of the carbon-carbon bonds (structures), the production procedure, structural change at high temperatures, nanotexture, and time of



**FIGURE 1.2 Classification of Carbon Materials**

appearance [1,2]. Carbon materials have been named from different viewpoints. Structurally, they can be divided into diamond, graphite, fullerenes, carbynes, glass-like carbons, etc., and by production procedure into artificial graphite, intercalation compounds, activated carbons, carbon/carbon composites, etc. In Figure 1.2, some representative carbon materials are shown. Those in bold italics are listed in relation to carbon families classified on the basis of carbon-carbon bonds, together with some information on the diversity in each family.

Based on the nature of the carbon-carbon bonding, four carbon families have been defined and named after representative carbon materials: the diamond family constructed by C-C bonds based on  $sp^3$  orbitals, the graphite family with bonds based on planar  $sp^2$  orbitals, fullerenes on curved  $sp^2$  orbitals, and carbynes on  $sp$  orbitals. In the graphite and fullerene families, the two  $\pi$  electrons per one carbon atom have a pronounced influence on the properties.

Commonly known carbon materials are shown in Figure 1.2. Most carbon materials that have been produced on an industrial scale belong to the graphite family. The fundamental structural unit is a stack of layers of carbon hexagons, i.e. graphite-like hexagonal carbon layers. These hexagonal carbon layers have strong anisotropy because of strong covalent bonding due to  $sp^2$  orbitals in the layer, but weak bonding of van der Waals force between  $\pi$  electron clouds of stacked layers.

When these layers are large enough, they stack with specific regularity: ABAB stacking results in graphite crystals belonging to the hexagonal crystal system [3]



and ABCABC stacking results in graphite crystals belonging to the rhombohedral crystal system [4]; the latter crystals being in metastable phase under atmospheric pressure. When the layers are too small, there is no stacking regularity even though they stack in parallel. The structure, where layers are just stacked without regularity, cannot be called graphite and has been named *turbostratic* [5]. It is known to be common in various layered compounds, such as clays. Turbostratic stacking is also metastable under normal conditions, around room temperature under atmospheric pressure, and it is thought to be stabilized by the presence of hydrogen and other foreign atoms, which bond to carbon atoms located at the edges of the layers and also by dangling bonds with neighboring layers.

The spacing between two layers that stack without regularity (turbostratic stacking), is larger than that of graphitic stacking. Interlayer spacing of graphite crystals has been accurately determined to be 0.3354 nm [6]. Interlayer spacing of turbostratic stacking is reported to be 0.344 nm [7], but now it is understood not to be a unique value, because of the presence of foreign atoms at the edges of layers. A turbostratic structure is commonly observed after the carbonization of many carbon precursors, because carbonization occurs at temperatures as low as 700–1300 °C. By heat treatment at higher temperatures, carbon layers grow in both directions, parallel to the layers (increase in the crystallite size  $L_a$ ) and perpendicular to the layers (increase in the thickness of parallel stacking, which is measured as crystallite size  $L_c$ ). This crystallite growth was known to depend strongly on carbons prepared at low temperatures, and it was proposed to classify carbons into two groups, graphitizing and non-graphitizing carbons [7], later named graphitizable and non-graphitizable carbons [8] or soft and hard carbons [9]. However, this classification into graphitizing and non-graphitizing is not critical, mainly because carbon materials with a variety of nanotextures have been developed and they show very different behaviors under high-temperature treatment.

During crystallite growth, the average interlayer spacing, usually measured by X-ray powder diffraction analysis, increases gradually with increase in heat treatment temperature, so that graphitic stacking with the spacing of 0.3354 nm occurs randomly in the crystallite with turbostratic stacking, as shown schematically in Figure 1.3 for a certain moment during heat treatment.

The development of graphitic stacking (graphitization degree) can be determined exactly by the probability of incidence in neighboring layers  $P_1$ , which can be done by Fourier analysis of the X-ray powder pattern [10]. Since the procedure to determine  $P_1$  is not simple, however, the average interlayer spacing,  $d_{002}$ , is often used as a convenient parameter for the graphitization degree, which can be measured from the diffraction angle of 00 $l$  diffraction lines. In Figure 1.4, change in the average  $d_{002}$  with heat treatment temperature is shown for different carbon materials, demonstrating how widely the behavior of carbon materials varies.

From measured  $d_{002}$ , different parameters, such as  $p$  and  $g$ , have been proposed to evaluate the graphitization degree, by making various assumptions [7,11,12]. However, the value  $d_{002}$  itself is now used as a measure of graphitization degree, often coupled with the crystallite sizes of  $L_c$ ,  $L_a$ , and  $L_c(112)$ . The specifications for