Chapter 1

Introduction

1.1 Biomass and carbon

Biomasses have been used as the precursors for charcoals since prehistoric era. Till now, they are still important precursors for activated carbons; activated carbons derived from coconut shell and wood are principally employed in various industrial fields. The rapid development in modern sciences and industries demands the exact control in functionalities of the activated carbons. In the field of carbon materials, the control in pore structure, not only pore content and their sizes but also pore morphologies, and the modification of pore walls was strongly required for activated carbons. These trends promoted the development of new techniques for the production of carbon materials, such as chemical vapor deposition, hydrothermal carbonization, isostatic forming process, and pore structure control by template-assisted carbonization and polymer blending processes[1]. To control functionality of the carbon materials, the formation of the composites of carbon materials with other materials, such as carbon fiber reinforced polymers (CFRPs), was demonstrated and expanded the application fields of carbon materials widely. It has also been reported that the doping of foreign atoms, such as N, B, S, etc., into the structure of carbon is often effective for enhancing the functionalities of carbon materials[2-3]. It has been pointed out that the renewable and sustainable resources for the materials are essential for realizing a low-carbon society. Biomasses are recently reassessed as the carbon precursors. From a chemical perspective, some of them are much advantageous for foreign atom doping and have beneficial nanotexture that is possible to be inherited to the resultant carbon materials. In addition, from an environmental

and economical perspectives, biomasses are renewable, sustainable, and carbon-neutral, and the increasing amount of waste biomasses appeals for some effective and safe ways to re-use.

According to International Union for Pure and Applied Chemistry (IUPAC), biomass is defined as "material produced by the growth of microorganisms, plants or animals"[4]. The plant-origin biomass is often called lignocellulose (lignocellulosic biomass) composed of three main natural polymers of cellulose $(C_6H_{10}O_5)_x$ and hemicellulose $(C_5H_8O_4)_m$ with lignin $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9\text{-}1.7}]_n$. It is often classified into virgin biomass, waste biomass and energy crops. Virgin biomass includes all naturally occurring terrestrial plants, such as trees, bushes and grasses. Waste biomass is produced as a low-value byproduct of various industrial processes, including agriculture (such as corn stover, sugarcane bagasse, straw, shell, etc.), forestry (such as sawdust and paper-mill discards, etc.) and daily-life activity (such as waste paper and tissue, etc.). Energy crops are produced to serve as a raw material for second generation biofuels. The estimated biomass production in the world is approximately 100 billion metric tons per year, about half in the ocean and half on land.

Biomass, particularly lignocellulosic biomass, has been used for the industrial production of activated carbons. Their carbonization and activation have been reviewed in various review articles[5-23] and books[1-3].

In this book, biomasses are classified into three on the basis of the polysaccharide composing of the biomass, as shown in Fig. 1-1.

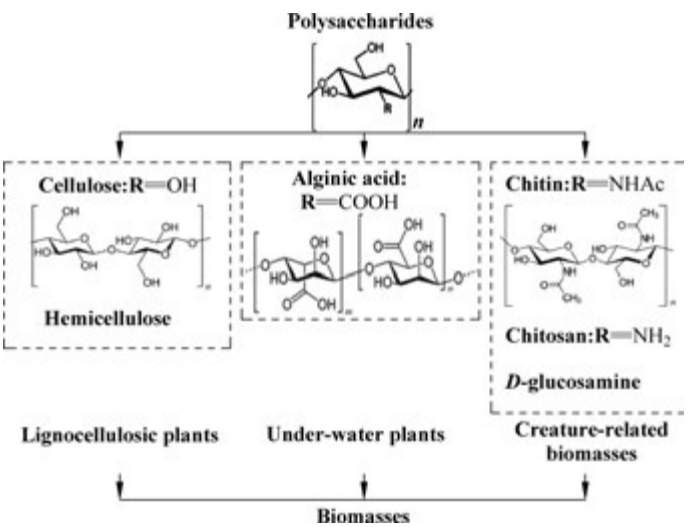

Fig. 1-1 Biomasses based on polysaccharides

(1) Lignocellulosic plants composing of mainly cellulose with hemicellulose and lignin;

(2) Under-water plants (aquatic plants) composing of alginic acid;

(3) Creature-related biomass composing of chitin.

Most of the biomasses are polymers consist of linearly linked glucose units and with different side groups R. Cellulose, which has -OH at the R-position, is main component of most of the plants, woody plants and herbaceous plants, together with hemicellulose and lignin (lignocellulosic plants). Alginic acid having -COOH at the R-position is main component of under-water plants, and chitin having-NHCOOH (-NHAc) at the R-position is the main component of creature-related biomasses.

1.2 Purpose and concept of this book

The main purpose of this book is to survey what have been done on biomasses already, both on the derivation of carbon materials and on their applications related to modern science and technology. For the coming carbon-zero society, the biomasses will occupy an important position as carbon precursors, mainly because of their carbon neutrality. The fabrication of activated carbons from some biomasses has a long history. For responding to the requirements from modern applications, such as energy storage devices, CO_2-capture, microwave shielding, etc., the more-detailed investigations are strongly demanded using modern techniques on the characterization of structure and properties, associating with the marked enhancement in the functionalities of the resultant carbons. To respond these requirements, numerous investigations have been done and numerous literatures have been published in a number of scientific journals. To survey all literatures, the scientists are insisted to spend fug times and efforts. Moreover, some of literatures contain basic errors and/or deficits of satisfactory deepness in science and engineering on carbon preparation and applications. Therefore, this book is planned to summarize what have been done on carbonization and activation of biomasses and what fields of applications have been covered for the biomass-derived carbons.

In this book, the preparation of the carbon materials from biomasses is focused on those for the new applications. Their applications are categorized into two, *i.e.*, energy storage and environment remediation. The former includes the applications to the electrode materials of supercapacitors, rechargeable batteries and fuel cell, methane storages, etc. and the latter includes the application to the adsorptive removal of various pollutants, CO_2-capture, capacitive de-ionization, microwave shielding, etc. As for the

conventional activated carbons, their carbonization/activation conditions and their applications were already explained and discussed in various reviews and books, as mentioned above.

The concept and construction of this book is summarized in Fig. 1-2. Lignocellulosic biomasses, composed of cellulose, hemicellulose and lignin, are existed as so many genera on the earth. Here, they are classified into two, woody plants and herbaceous plants. In addition, their parts, such as shell, stalk, stones etc. are separately supplied as the agricultural wastes and the industrial by-products or wastes in large kinds and amounts. Under-water plants (aquatic plants), based on alginic acid are obtained as different seaweeds and microalgae. The creature-related biomasses of crustaceans, microorganisms, bones, and scales are composed of chitin and are supplied as by-products and wastes. In addition, swage sludges and fly ashes, which are produced in wastewater-treatment plants and as a residue of fuel combustion, respectively, are also biomasses.

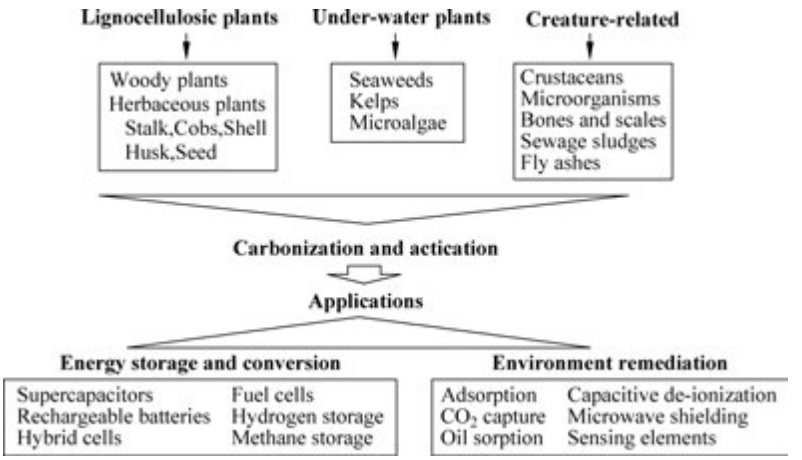

Fig. 1-2 Concept of this book

Sectioning in this book is shown in Fig. 1-3. Lignocellulosic plants themselves and their parts, such as shells, peels, beans, etc. are explained separately in **Chapter 2** and **Chapter 3**, respectively, by focusing how to convert them to carbon materials (carbonization and activation) and what applications are studied on the resultant carbons. Some plants grown under water (under-water plants or aquatic plants) are composed from alginic acid, which behave differently from lignocellulosic plants and so they are explained in **Section 2.3**. Some biomasses (such as crab shell, bacteria, seaweeds, animal bone and fish scales) contain chitin as a main component, of which conversion to carbon materials

are explained in **Chapter 4**, together with other biomasses, such as sewage sludges, manures, fly ashes, which are difficult to be classified into the above-mentioned biomasses. In each section, sustainability of the biomass for carbon precursors with their occurrence in nature are shortly explained and then their carbonization and activation are summarized. The applications of the carbons derived from each of biomasses are presented from two aspects, energy storage and conversion, and environment remediation.

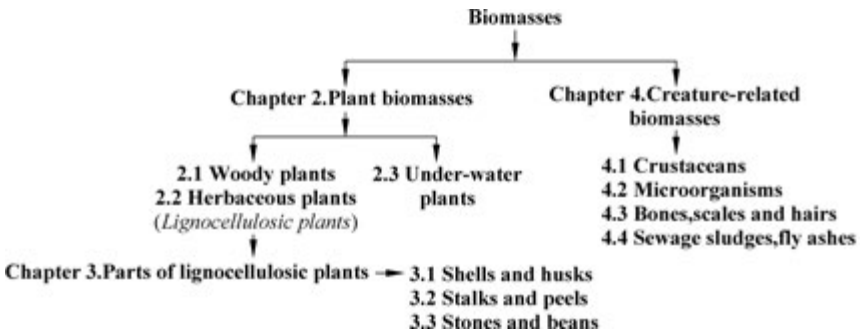

Fig. 1-3 Sectioning in this book

1.3 Fundamentals

Before discussing on biomass-derived carbons, fundamentals of carbon materials science are briefly explained here, emphasizing the diversity of carbon materials in structure and textures with various scales. On more detailed explanation and discussion on carbon materials, the readers are suggested to refer to fundamental books written by the current authors (M.I. and F.K.)[2-3].

1.3.1 Carbon materials

a) Classification

Numerous kinds of carbon materials have been synthesized and widely used in various fields of industries. These carbon materials are proposed to be classified on the basis of chemical bonds of constituent carbon atoms using sp^3, sp^2 and sp hybrid orbitals[24]. The sp^2 hybrid bonding of carbon atoms results in two structures: flat layers composed of six-membered carbon rings, which have so far been represented by graphite but now are typified by graphene, and curved layers created by introducing five-membered carbon rings into six-membered rings, as occurs in fullerenes. Carbon layers

composed of sp^2 orbitals, both flat and curved, are intrinsically anisotropic and have π-electron clouds on both sides of the layer, and these anisotropic layers create the broad diversities in the structure and properties of the carbon materials. Carbon nanotubes can be placed in between fullerene and graphene, because the tips of the tube include five-membered rings (fullerene-like) and its wall is composed of six-membered rings (graphene-like) though it is rolled up. A classification of carbon materials based on hybrid bonds is presented, together with the diversities of the materials, in Fig. 1-4.

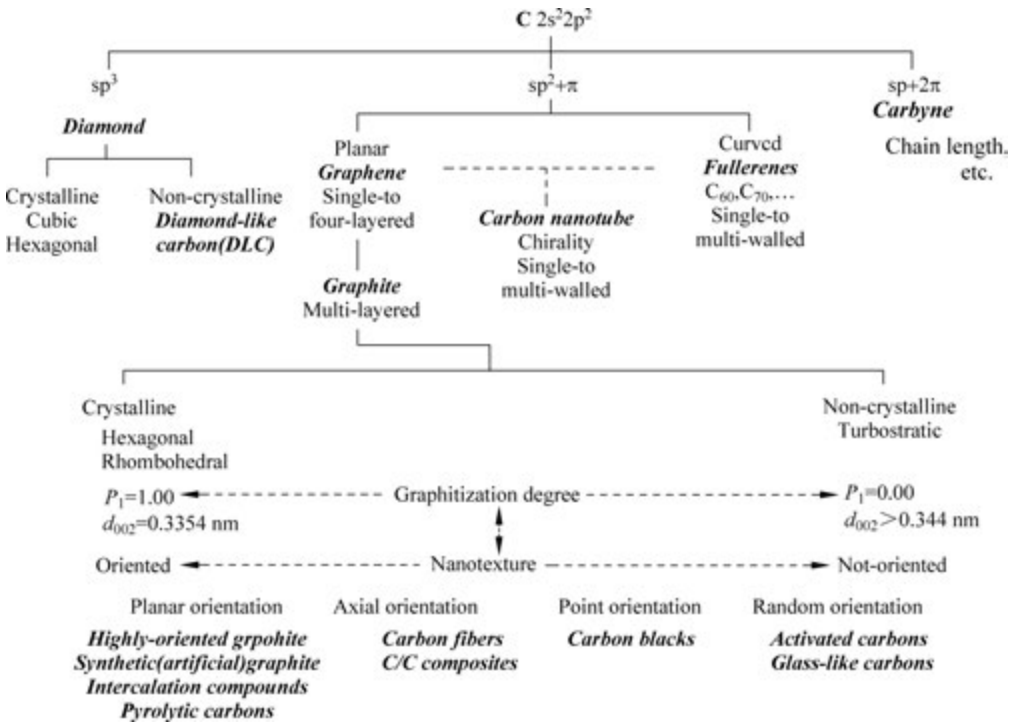

Fig. 1-4 Classification and diversities of carbon materials

Due to the anisotropic nature and the presence of π-electron clouds in the carbon materials composed mainly of sp^2 hybrid orbitals, the number of carbon layers stacked in parallel has strong influence on their properties. The importance of the number of stacked layers has been pointed out on carbon nanotubes and fullerenes, and now on graphene[25]. In addition, the lateral size of layers and their stacking regularity make the diversity of carbon materials widened. An infinite number of large-sized layers stacked with a regularity has been called graphite, which is crystalline and strongly anisotropic in structure, consequently strongly anisotropic in properties. In contrast,

random aggregation of the units of irregularly stacked small layers results in so-called amorphous carbon (disordered carbon), which is isotropic in properties with high mechanical strength and high hardness. In between crystalline graphite and non-crystalline amorphous carbon, various graphite-related materials having the structure of different degrees of graphitization (proportion of regular stacking) and layer sizes have been produced in industries and used as important industrial materials.

b) Pyrolysis, carbonization and graphitization

Most of carbon materials are produced from organic precursors, such as pitches, organic polymers and biomasses, *via* heat treatment at high temperatures in inert atmosphere. In Fig. 1-5, chemical and crystallographic structures and processes are shown as a function of heat treatment temperature (HTT); decomposition of organic molecules accompanying the evolution of light and heavy aromatic molecules (pyrolysis process), and subsequent growth of basic hexagonal carbon layers accompanying the evolution of CO, CO_2, CH_4 and H_2 (carbonization process) occur up to about 2500℃, followed by further growth of carbon layers associated with improvement of their stacking regularity above 2500℃ (graphitization process). In most cases, the pyrolysis and carbonization occur simultaneously and so difficult to differentiate these two processes.

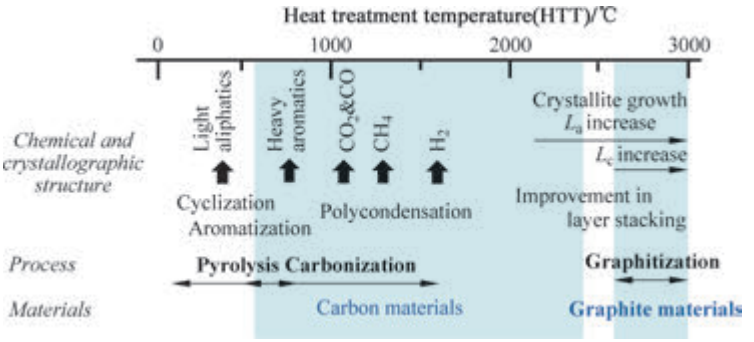

Fig. 1-5 Schematic illustration of the changes in chemical and crystallographic structures with heat treatment temperature (HTT) for an organic carbon precursor

Carbonization proceeds after pyrolysis of organic precursors at the temperature range from 600℃ to 2000℃, in which the basic structural units (BSUs) are formed and their aggregation scheme (nanotexture) is established through polycondensation of six-membered carbon rings. This process is the most important in the production of various carbon and graphite materials, because the nanotexture established during this process governs the development of crystalline structure in the carbon materials during the

following graphitization process. During pyrolysis and carbonization processes, large shrinkage occurs due to large amount and rapid emission of gaseous species, associated with cracking in the resultant carbon particles in most cases. Therefore, the process of carbonization is usually performed separately from that of graphitization.

Carbon materials, except diamond, fullerenes and carbon nanotubes, are composed of flat layers with sp^2 hybrid orbitals and they consist of small units of layers stacked in parallel, which are called BSUs or crystallites. A lattice fringe image of TEM on an aggregation of some BSUs and a schematic illustration on a BSU are shown in Fig. 1-6(a) and (b), respectively. In the unit, two kinds of stacking regularity of layers are coexisted, regular and non-regular (random) stackings. The former is graphitic stacking (usually written as AB stacking) with the interlayer spacing d_{002} of 0.3354 nm (the same as natural graphite), while the latter is the random stacking with a slightly larger d_{002} as 0.342 nm, being called turbostratic stacking. These BSUs are strongly anisotropic in bonding nature; strong covalent bonding using sp^2 hybrid orbital along the layer and weak van der Waals-like bonding due to the interaction between π-electron clouds of the layers.

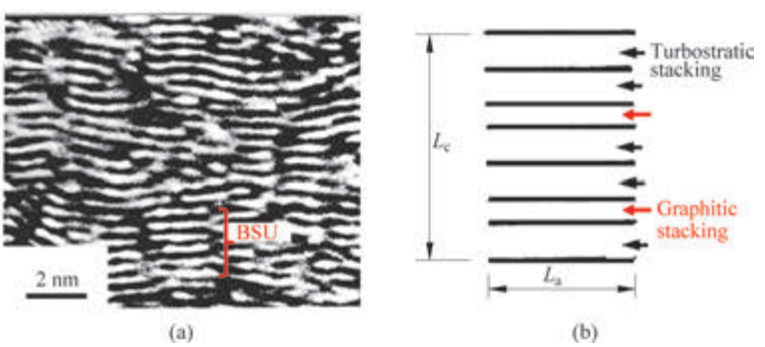

Fig. 1-6 Basic structural unit (BSU) of carbon materials: (a) lattice fringe image and (b) schematic illustration of a unit

The structure of the carbon materials is evaluated by X-ray diffraction (XRD). In Fig. 1-7(a) and (b), XRD patterns of natural graphite and a coke heat-treated at 1000℃ are shown by representing the highly crystalline structure, which is composed of large BSUs with graphitic stacking, and the amorphous carbon, which is composed of small BSUs with turbostratic stacking, respectively. Crystalline graphite displays sharp and strong diffraction peaks indexed by 002, 004 and 006 due to the diffraction from hexagonal carbon layers (001 diffraction peaks), associated with sharp peaks indexed by 100, 101, 112, etc. In contrast, the amorphous carbon displays broad and weak 001

peaks, 006 peak being undetectable, and broad peaks indexed by 10, 11. In turbostratic structure, the c-axis (perpendicular to the hexagonal carbon layer) cannot be defined, in other words, no index 1, and so the peaks as 101, 102, 112 are not observed. Since graphitic stacking has the interlayer spacing of 0.3354 nm, smaller than that for turbostratic stacking (larger than 0.342 nm), the interlayer spacing determined from the position (diffraction angle 2θ) of 001, mostly using 002 peak, is considered to be intermediate between these two spacings as a balance of graphitic and turbostratic stackings. The turbostratic stacking is thermodynamically metastable and so it tends to transform to stable graphitic stacking by high temperature treatment. This change in stacking regularity is evaluated by the average interlayer spacing d_{002} measured on the position of 002 peak. When the change of turbostratic to graphitic stackings occurs randomly, 001 diffraction profiles are almost symmetrical and shift gradually to high angle side, *i.e.*, gradual decrease in d_{002}. When this change occurs locally, in other words, some BSU changes to graphitic stacking but other BSUs do not, the observed 001 peaks are composed of two peaks at high and low diffraction angles (composite profile), usually the former being sharp and having d_{002} around 0.3354 nm while the latter being broad and shift to high angle side with increasing HTT. This structural change in carbon is called "graphitization".

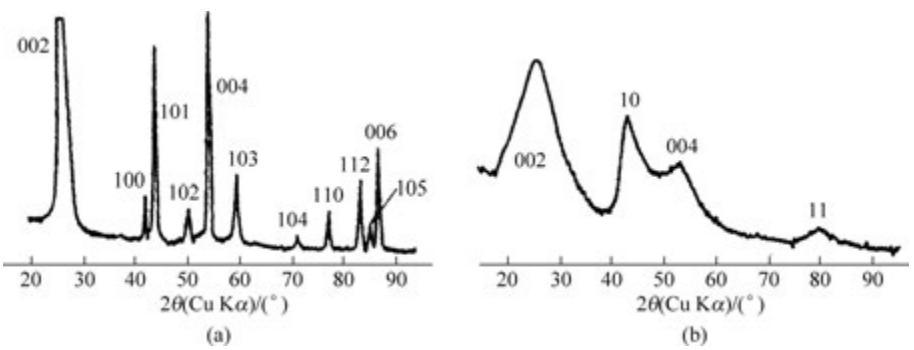

Fig. 1-7 X-ray diffraction pattern: (a) natural graphite and (b) petroleum coke heat-treated at 1000℃ (an amorphous carbon)

Above 2500℃, the change in crystalline structure, in other words, the development of graphite structure occurs mainly. The development of graphite structure is evaluated by the analyses of XRD[26-27]. In BSUs formed during carbonization, turbostratic stacking with interlayer spacing of about 0.342 nm is randomly changed to graphitic regular stacking with the spacing of 0.3354 nm (the spacing in the graphite crystal) with

increasing heat treatment temperature (HTT) above 2000℃, which is evaluated as the decrease in average interlayer spacing d_{002} by XRD, associated with the growth of BSU sizes (crystallite sizes) along a-axis and c-axis, L_a and L_c, respectively. The change in d_{002} with HTT depends strongly on the materials after carbonization (carbon materials). In Fig. 1-8, the changes in these parameters with HTT are shown for various carbon materials. In a needle-like coke, d_{002} decreases quickly to approach the value of graphite crystal (0.3354 nm) and L_c and L_a grow rapidly. In glass-like carbon, in contrast, almost no decrease in d_{002} and no appreciable growth of L_c and L_a are observed even after 3000℃ treatment, *i.e.*, no development of graphite structure. Carbon blacks exhibit intermediate behaviors strongly depending on their particle size: large-sized thermal black shows more structure improvement than small-sized furnace black.

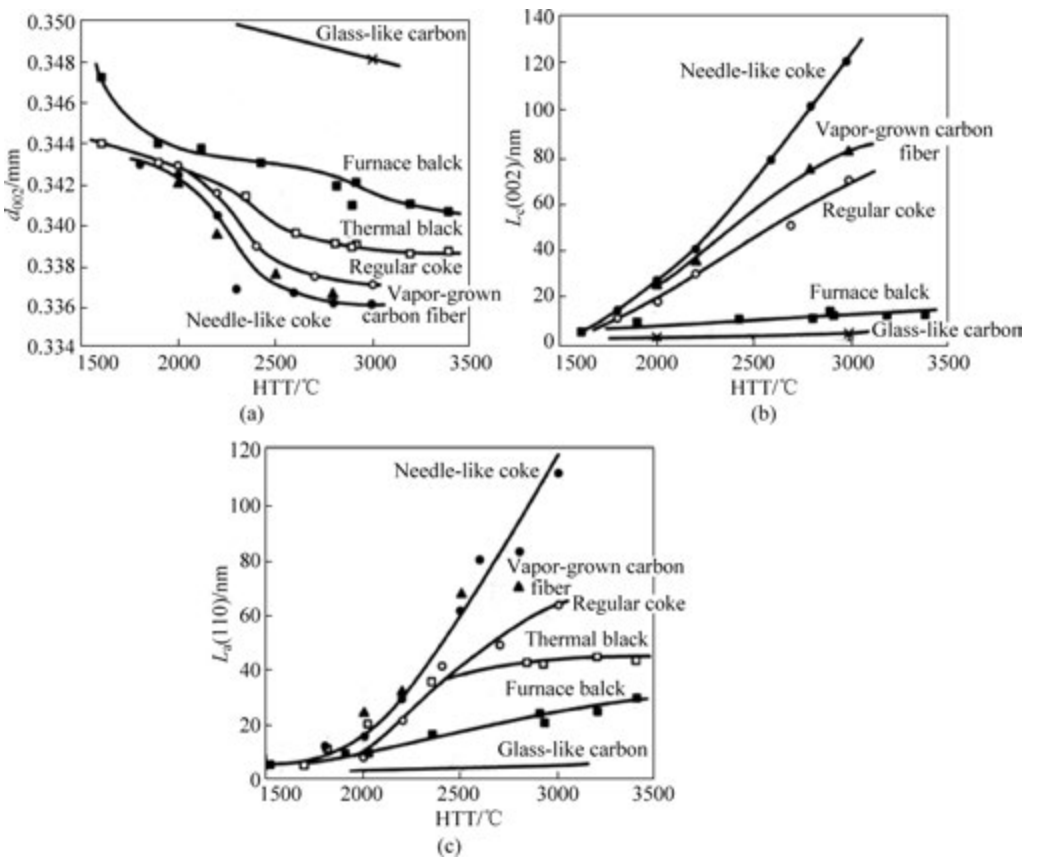

Fig. 1-8 Changes in XRD parameters with HTT on various carbon materials: (a) d_{002}, (b) L_c measured from 002 diffraction peak, and (c) L_a from 110 peak