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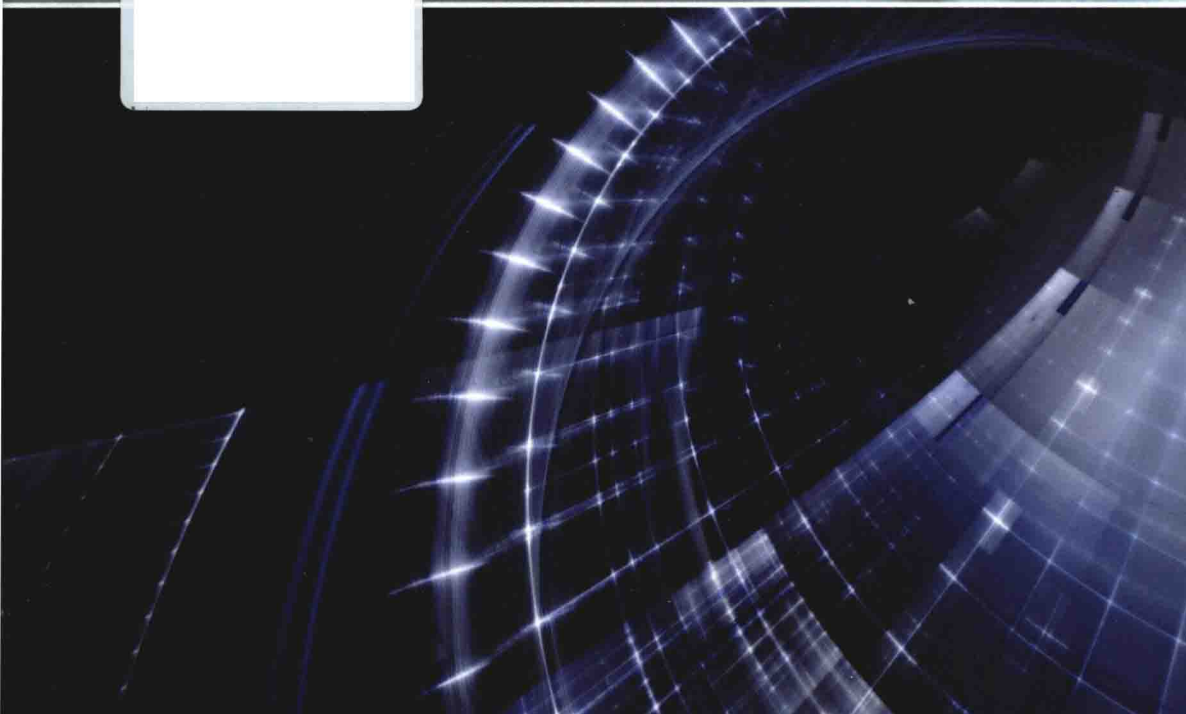

NANOCRYSTALLINE MATERIALS

THEIR SYNTHESIS-STRUCTURE-PROPERTY RELATIONSHIPS AND APPLICATIONS

SECOND EDITION

Edited by

SIE-CHIN TJONG

Nanocrystalline Materials
Their Synthesis-Structure-Property Relationships and Applications

Second Edition

Edited by

Sie-Chin Tjong

Department of Physics & Materials Science,
City University of Hong Kong,
Hong Kong

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AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier
32 Jamestown Road, London NW1
7BY, UK 225 Wyman Street, Waltham, MA
02451, USA

First Edition 2006
Second Edition 2014

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-12-407796-6

This book has been manufactured using Print On Demand technology. Each copy is produced to order and is limited to black ink. The online version of this book will show color figures where appropriate.

Transferred to Digital Printing in 2013

Nanocrystalline Materials

Preface

Nanocrystalline materials with different shapes, morphologies, and structures possess excellent chemical, physical, or mechanical properties compared to their microcrystalline counterparts. Thus the synthesis, development, and material characterization of novel nanocrystalline materials have attracted the research interest of chemists, physicists, and materials engineers. This book reviews the latest synthesis, development, and characterization of nanocrystalline materials, as well as the potential use of such novel materials for bioimaging, drug delivery, electronic device, solar cell, and structural engineering applications. The chapters were written by leading scientists in their respective subject fields. The purposes are to provide the readers, including all scientists, engineers, and graduate students working in academia and industry, new information and knowledge on nanocrystalline materials to enhance their understanding and innovation.

The first edition of this book was published in 2006. The synthesis and characterization of nanomaterials have developed very rapidly in the past 7 years. Therefore, I have removed a few chapters of the first edition which have become a little dated. These include: Chapter 1 (Solution route to semiconducting nanomaterials), Chapter 2 (Synthesis architecture of inorganic nanomaterials), Chapter 4 (Fabrication and structural characterization of ultrathin nanoscale wires and particles), Chapter 5 (Synthesis and characterization of various one-dimensional semiconducting nanostructures), and Chapter 7 (Synthesis of hyberbranced conjugative polymers and their applications as photoresists and precursors for magnetic ceramics).

The contents of this second edition have been carefully revised and updated to expand coverage of several new key topics relating to the energy, biomedical science, and electronic device. Chapter 1 presents the synthesis of multiwalled carbon nanotubes using bamboo charcoal as one of the precursor materials. Bamboo charcoal is an eco-friendly biocarbon obtained by pyrolyzing bamboos at high temperatures. Bamboo charcoal contains a considerable amount of mineral elements, acting as effective catalysts for growing carbon nanotubes at high temperatures. This eliminates the use of transition metal nanoparticles commonly used for the synthesis of nanotubes. Chapter 2 addresses the structure and property of one-dimensional (1D) ZnO nanowire array for use as the photoanode of dye-sensitized solar cells. ZnO possesses high electron mobility, low crystallization temperature, and anisotropic growth behavior rendering it a very promising candidate for the flexible photoanode. Chapter 3 reviews the fundamentals and the most recent developments in the preparation methods, basic property characterizations as well as the applications of 1D nanostructured materials in the energy transformation into electricity by solar cells, piezoelectric generators, thermal conversion devices and energy storage in fuel cells, lithium ion batteries, and supercapacitors. Chapter 4 concerns the synthesis, property, and application of lanthanide-doped fluoride nanocrystals. Such doped nanoparticles can be excited with near-infrared (NIR) radiation, thereby effectively converting the NIR light to ultraviolet and visible regions, a process known as upconversion. Upconversion generally causes the emission of higher energy photons through the sequential absorption of lower energy photons. Lanthanide-doped upconversion nanoparticles with appropriate surface modification find a wide range of biomedical applications, including biodetection, cancer therapy, and bioimaging. Chapter 5 is the revised text of the first edition, concerning molecular self-assembled monolayers on hydrogen-terminated silicon. The self-assembly approach facilitates the fabrication of ultrathin films using organic molecules as the building blocks, thereby permitting the design of new functional nanodevices at the supramolecular level. Chapter 6 introduces the synthesis and application of polymer nanocomposite as a dielectric layer for flexible organic electronics. Novel dielectric material based on aluminum titanate nanoparticles functionalized with *n*-octadecylphosphonic acid and the poly(4-vinylphenol) matrix exhibits superior electronic performance in both the n-type and p-type organic thin film transistors. From the flexibility test, such devices are mechanically stable and environmentally robust. Chapter 7 discusses the use of specific types of nanomaterials, such as semiconductor quantum dots, magnetic nanoparticles, layered double hydroxides, organic nanoparticles, and metal nanostructures, as the vehicles for drug delivery systems. Chapter 8 presents the fabrication, structure, and mechanical properties of aluminum and magnesium-based composites reinforced with ceramic nanoparticles. The mechanical performance of metal matrix nanocomposites depends greatly on the attainment of homogeneous dispersion of ceramic nanoparticles in the metal matrix. Particular attention is paid to the processing techniques for achieving uniform dispersion of nanoparticles in the composites and their structure−property relationships. Chapter 9 gives an introduction to the use of ceramic, organic, metal, and carbon nanoparticles to enhance dielectric permittivity of polymers. This chapter describes the fundamental aspects, processing techniques, and the underlying mechanisms for attaining high permittivity in polymer nanocomposites. Chapter 10 reports the synthesis and mechanical properties of graphene−polymer nanocomposites. Two-dimensional graphene exhibits exceptionally high elastic modulus and mechanical strength. It is an ideal nanomaterial to reinforce polymers for fabricating structural composites at very low filler contents. The chapter presents the strategies used to improve the mechanical performance of the polymer nanocomposites. Finally, Chapter 11 discusses the electrical conducting behavior of polymers filled with carbonaceous nanomaterials, including carbon nanofibers, carbon nanotubes, and graphene nanoplatelets. Under the application of an electric field, the percolating nanocomposites exhibit nonlinear electrical conductivity and Zener tunneling effect.

Sie Chin Tjong, CEng CSci FIMMM
City University of Hong Kong, Hong Kong and
King Abdulaziz University, Jeddah, Saudi Arabia

List of contributors

Xianfeng Chen Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Kowloon Tong, Hong Kong SAR, PR China

Zhi-Min Dang Laboratory of Dielectric Polymer Material and Device, Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science & Technology Beijing, Beijing, China

Ning Han Department of Physics and Materials Science, and Centre for Functional Photonics (CFP), City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, PR China

Su-Ting Han Department of Physics and Materials Science and Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, PR China

Linxiang He Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, PR China

Johnny C. Ho Department of Physics and Materials Science, and Centre for Functional Photonics (CFP), City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, PR China

Juncai Jia Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong, China

Chen-Hao Ku Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

Wen-Pin Liao Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

V.A.L. Roy Department of Physics and Materials Science and Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, PR China

Hiroyuki Sugimura Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto, Japan

Sie Chin Tjong Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, PR China; Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

Feng Wang Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, PR China

Hongli Wen Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, PR China

Chun-Te Wu Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

Jih-Jen Wu Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

Li Yan Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Kowloon Tong, Hong Kong SAR, PR China

Ye Zhou Department of Physics and Materials Science and Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, PR China

Jiangtao Zhu School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ

Contents

1 Preparation, Structure, and Application of Carbon Nanotubes/ Bamboo Charcoal Composite

Jiangtao Zhu[1], Juncai Jia[2] and Sie Chin Tjong[3]

[1]School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, [2]Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong, China, [3]Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

1.1 Introduction

Naturally grown plants, such as wood and bamboo, have unique and sophisticated structures after evolution by mother nature for ages. Functional materials can be fabricated by mimicking the hierarchically build structural morphologies of renewable bioresource materials. Bamboo plants are indigenous to East Asia but are now planted in worldwide subtropical regions. The total area of bamboo forest is about 22 million ha (1 ha is 10,000 m^2), accounting for about 1.0% of the total global area of forest [1]. Although the total forest areas in many countries decrease drastically in recent years, but the bamboo vegetation increases at a rate of 3% annually. There are about 1200 types of bamboo globally. As bamboo does not need fertilizers, or pesticides, bamboo products are considered as inexpensive and eco-friendly materials. Once the bamboo is carbonized or pyrolyzed, bamboo charcoal with profuse porosity is produced. The bamboo charcoal has attracted intense attention in the past few years due to their attractive properties, including absorption, catalyst support, medical electrode, and agricultural function [2–16].

Carbon nanotubes (CNTs) exhibit excellent mechanical, thermal, and electrical properties having many functional applications [17–19]. CNTs are synthesized in large quantities by means of chemical vapor deposition (CVD) of hydrocarbon gases using transition metal or rare earth metal catalysts [18]. However, those heavy metals are toxic and pose serious problems to human health and the environment. In addition, loose CNTs are unsuitable for some applications, such as gas phase catalysis and liquid phase absorption [20]. In this regard, the successful synthesis of CNTs from bamboo charcoals is considered of technological importance. This is because bamboo charcoals containing many minerals can serve as effective

Nanocrystalline Materials. DOI: http://dx.doi.org/10.1016/B978-0-12-407796-6.00001-4

catalysts for the nucleation and growth of nanotubes. Accordingly, CNTs can be grown on a charcoal supporting material with eco-friendly characteristic.

In this chapter, the morphology, structure, and composition of the bamboo charcoal are first addressed. The processes for growing CNTs on the bamboo charcoal surfaces via CVD and arc-discharge techniques are reviewed. The role of extra catalyst added to the bamboo charcoal on the growth of CNTs at low temperatures is also discussed. Furthermore, bamboo charcoal is an excellent biomass adsorbent that has strong adsorption ability for organic pollutants and heavy metal ions. The applications of CNT/bamboo charcoal for water purification and hydrogen storage are also presented.

1.2 Bamboo Charcoal

1.2.1 Morphology, Phase, and Compositions of Bamboo Charcoal

The bamboo charcoal is usually obtained by pyrolysis bamboo in an inert atmosphere at temperatures above 700°C. The process is also termed as the carbonization in the preparation of activated carbon. During carbonization, biological bamboo releases contained water and organic gases followed by the reconstruction of carbon structure. Figure 1.1 shows typical thermogravimetry analysis (TGA) of several bamboos in a nitrogen atmosphere from room temperature to 900°C. The first mass loss at temperatures below 100°C is related to water vaporization. At 80–250°C, the mass loss of the bamboo remains stable. Then the mass drops drastically at 250–400°C due to the fast thermal decomposition of cellulose, lignin, and semicellulose. Large CO_2 and CO are released at this stage. Above 400–900°C, the mass decreases slowly. This final stage is mainly associated with the carbonization during which the aromatic rings rearrange into charcoal [21]. Four types of bamboos as shown in Figure 1.1 are used for the TGA, i.e., *Phyllostachys edulis*, *Dendrocalamus*, *Dendrocalamus brandisii*, and *Bambusa inteimedia*. Clearly, the most popular *P. edulis* has a slight different thermal property compared with other types of bamboos. Even *P. edulis* from different locations in China displays different behaviors. The *B. inteimedia* has a highest residue after the TGA process.

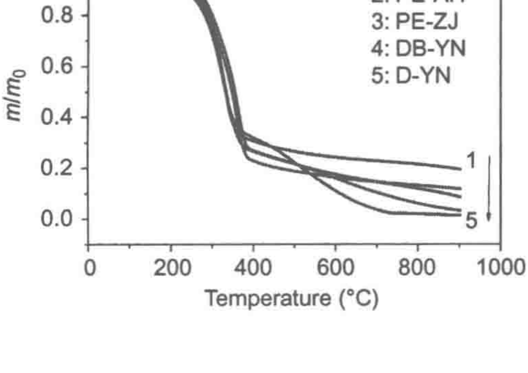

Figure 1.1 TGA of five types of bamboo: (1) BI-YN, *Bambusa*; (2) PE-AH, *Phyllostachys*; (3) PE-ZJ, *P. edulis*; (4) DB-YN, *D. brandisii*; and (5) D-YN, *Dendrocalamus*. YN, AH, and ZJ refer to Yunnan, Anhui, and Zhejiang provinces (China) where the bamboos obtained.

Generally, there is a significant volume shrinkage during the pyrolysis, however, the tubular structure of bamboo is still retained. Scanning electron microscopy (SEM) cross-sectional and lateral views show the porous feature of the bamboo charcoal carbonized at 1000°C [22] (Figure 1.2). The bamboo charcoal still retains porous nature of original bamboo. Mineral aggregates are found on the walls of vessel lumen. Jiang et al. [23] studied the shrinkage of the bamboo at different carbonization temperatures. The scaffolding of the bamboo charcoal remained the same as original bamboo, however, the microstructure of the bamboo was slightly changed during the shrinkage. The shrinkage ratios of the bamboo were about 21, 38, and 40% at 500, 750, and 1000°C, respectively. Jiang et al. also found that the wall of the parenchyma, the basic unit inside the bamboo, became rough. The outer surface of the bamboo became smooth and the whole bamboo charcoal became hard. Very recently, Zhu et al. studied the morphologies of bamboo charcoal treated at temperatures up to 1500°C. The morphologies of bamboo charcoal carbonined at 1000–1500°C retain porous feature of fresh bamboo [24]. Moreover, the bamboo charcoal exhibits a wide range of pore distribution from <1 nm to 1 μm based on the mercury porosimetry measurements (Figure 1.3). The charcoal has several dominant pore sizes (at 30, 200, 2000, and 20,000 nm), confirming hierarchical pore feature of the bamboo charcoal. The total volume of the mercury absorbed by the bamboo charcoal is about 1.7 mL/g.

The bamboo charcoal usually contains mainly carbon with a small amount of impurities. The X-ray diffraction (XRD) patterns of several bamboo charcoals prepared at

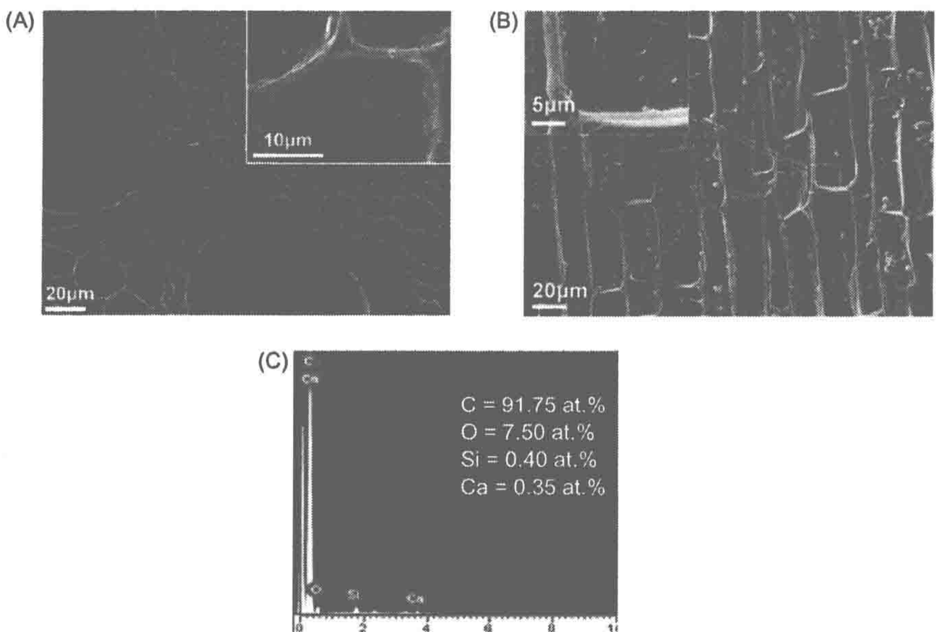

Figure 1.2 SEM images showing the (A) cross-sectional and (B) lateral views of raw bamboo biotemplate after pyrolysis and (C) corresponding EDS spectrum.
Source: Reprinted from Ref. [22] with permission of Wiley.

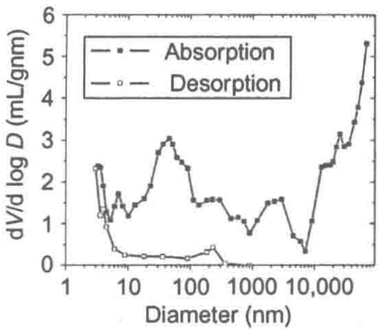

Figure 1.3 The pore structure of bamboo charcoal (*P. edulis*) revealed by absorption/desorption of mercury porosimetry.

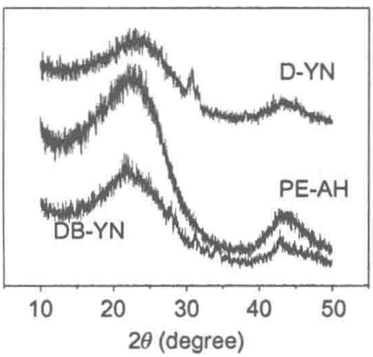

Figure 1.4 XRD patterns of D-YN, *Dendrocalamus*; PE-AH, *P. edulis*; and DB-YN, *D. brandisiss*. YN and AH refer to Province of Yunnan and Anhui (China), respectively, where the bamboos obtained.

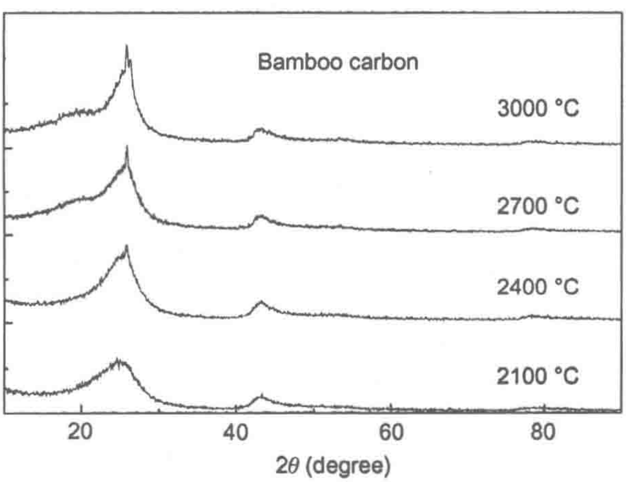

Figure 1.5 The XRD profiles of bamboo charcoal after heat treatment at different temperatures.
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800°C are shown in Figure 1.4. There are only two broad peaks located at 22 and 43°, corresponding to C_{0002} and C_{0004} reflections of carbon, respectively. Those broad peaks confirm they are mainly amorphous carbon. Chen et al. [25] (Figure 1.5) studied graphitization behavior of bamboo charcoal after carbonization up to 3000°C using XRD. The d_{0002} spacing of the bamboo charcoal decreased while the apparent graphite crystallite size L_c (0002) increased with the increase of graphitization temperatures. However, even after heat treatment at 3000°C, the d_{0002} and L_c (0002) values were only about