Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 61 (2007) 1839–1844
materials letters
www.elsevier.com/locate/matlet

Mechanical properties, microstructure and histocompatibility of MWCNTs/HAp biocomposites

Aimin Li [a,b,*], Kangning Sun [a,b], Weifang Dong [c], Dongmei Zhao [d]

[a] Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education Shandong University, Jinan Shandong Province, 250061, PR China
[b] Engineering Ceramics Key Laboratory of Shangdong Province, PR China
[c] Shandong Institute of Light Industry, Jinan Shandong Province, 250100, PR China
[d] The Second Hospital of Shandong University, Jinan Shandong Province, 250070, PR China

Received 14 May 2006; accepted 23 July 2006
Available online 18 August 2006

Abstract

In this paper, the authors mainly investigated the mechanical properties, microstructure and histocompatibility of multi-wall carbon nanotubes/hydroxyapatite (MWCNTs/HAp) composite prepared by two techniques. Compared with pure hydroxyapatite, the bending strength and fracture toughness of the composite are all improved, especially the latter whose increment exceeded 200%. XRD shows that the primary crystal phase of the composite is HAp together with the diffraction peaks of carbon nanotube. By SEM we found that there are more carbon nanotubes in the composite sintered in Ar, but there are much pores in it and the interface between the carbon nanotube and hydroxyapatite is not very strong. In vacuum, the diameter of carbon nanotube became larger (reported before) than that in Ar, but the interface between MWCNTs and HAp is very strong and there are less pores in the composite. From a pathologic micrograph we can draw conclusions as follows. When MWCNTs/HAp composite was embedded into the striated muscle of a big white mouse it produced a little stimulation to the tissue around it and there was no serious inflammation reaction, implying better histocompatibility. Both MWCNTs/HAp and ZrO_2/HAp composites can satisfy the condition of biomaterials but the histocompatibility of the former is much better than the latter.

Keywords: Mechanical properties; Microstructure; Multi-wall carbon nanotubes; Hydroxyapatite; Composite

1. Introduction

Carbon nanotubes (CNTs) are new-style materials which were developed for the last ten years. Carbon nanotubes were studied widely from the first radix carbon nanotube produced in 1991 [1–4]. The mechanical property of CNTs is very high. Its tensile strength is one hundred times higher than that of steel and its density is six to seven times lower as that of steel [5]. It can resist the erosion of strong acid and alkali and it cannot be oxided by oxygen when the temperature is lower than 973 K in air. It has a high aspect ratio, better electric property, definite magnetism and nanometer effect which belong to a one-dimensional nanostructure [6–8]. Thus, if we prepare the composite with CNTs and other engineering materials CNTs can strengthen and toughen the matrix. If the special nanometer of CNTs effect was utilized some functional material can be obtained. The theoretical study has shown that it is viable to fabricate composite with superhigh mechanical property by CNTs. The study of CNTs composite has become one of the most interesting research topics. The composite with CNTs such as CNTs/metal [9], CNTs/ceramic [10] and CNTs/polymer [11–13] has been prepared, but a few studies about CNTs/ceramic composite and its security have been reported. Hydroxyapatite (HAp) is one of the bioceramics with higher bioactivity, but it has lower mechanical property than human load-bearing bone and its low dependability needs to be strengthened and toughened. If CNTs and HAp were compounded we may obtain a composite with higher mechanical property, better biocompatibility and even definite magnetism and wave-absorbing properties. Thus, it is of importance and of

* Corresponding author. Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education Shandong University, Jinan Shandong Province, 250061, PR China. Tel./fax: +86 531 88392439.
E-mail address: liaimin@sdu.edu.cn (A. Li).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2006.07.159

Table1
Mechanical properties of the composites

Number	MWCNTs contents (wt.%)	Sintering temperature (°C)	Holding temperature (h)	Atmosphere	Bending strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
T0	0	1100	3	Air	25.85	0.32
T2	3	1100	3	Ar	61.43	0.761
T3	3	1100	3	Vacuum	66.11	2.401

application value to fabricate the composite and study its mechanical property, microstructure and biocompatibility. For comparison, a parallel study of ZrO_2/HAp composite was carried out at the same time in order to determine the histocompatibility of both composites.

2. Experimental

2.1. Raw materials

We adopt the chemical precipitation method to prepare HAp powder, and the materials and preparation method were discussed in detail before [14]. Multi-wall carbon nanotube: Shenzhen Nanotech Port Company, Limited, and its parameters are as follows: diameter: 40–60 nm; length: 0.5–500 μm; purity: 95%; agraphitic carbon: <3%; ash: ≤0.2 wt.%.

2.2. Preparation and dispersion of the composite powder, molding, sintering and post processing of the composites

Firstly, we used the chemical precipitation method to prepare the HAp powder. Secondly, we use the method of ultrasonic vibration to prepare the composite powder. Carbon nanotube and hydroxyapatite were dispersed respectively by the method of ultrasonic vibration in distilled water with a dispersant of sodium dodecyl sulfonate; when they were symmetrical dispersed we mix them together and continue ultrasonic vibration for 1 h; we remove the water and the multiple powder was obtained. Thirdly, the composite powder was made stable by cold press molding and cold isostatic compaction. The three sintering technology of the composite are as follows: (1) pressureless sintering in vacuum; (2) pressureless sintering in Ar; (3) pressureless sintering in N_2 .The samples were cut into standard bars by an Inner Circle Cutter, followed by mechanical properties testing of the composite.

2.3. Properties testing

The bending strength and fracture toughness are measured by the Microcomputer Control Universal Test Machine (CMT5105) with a loading rate of 0.5 mm/min. Phase analysis was carried out by XRD (D/max-3C, Cu-Kα) and the fracture surfaces were examined by SEM (S-520). The tissue was observed by an image analyzer (OLYMPUS BX50) after the samples were taken out.

2.4. Animal breeding and toxicity experiment

First, twelve mature big white rats whose avoirdupois is about 350 g were averagely separated into two groups. Then, cylindrical MWCNTs/HAp and ZrO_2/HAp composite samples that were strictly disinfected were embedded into the striped muscle. In the first, third, fifth, seventh and fourteenth day the samples and the tissue around the samples were taken out, with one rat spared. Some parts were cramped by 10% formaldehyde and then were observed by an image analyzer, and the other parts were put in a −80 °C refrigerator for molecular biology experiment (introduced in a special article).

3. The mechanical properties and microstructure of MWCNTs/HAp biocomposite

3.1. The mechanical properties of MWCNTs/HAp biocomposite

Table 1 shows the mechanical properties of MWCNTs/HAp composites. From the table we can see that the bending strength and fracture toughness of MWCNTs/HAp composites are all higher than pure hydroxyapatite and the increased quantum all

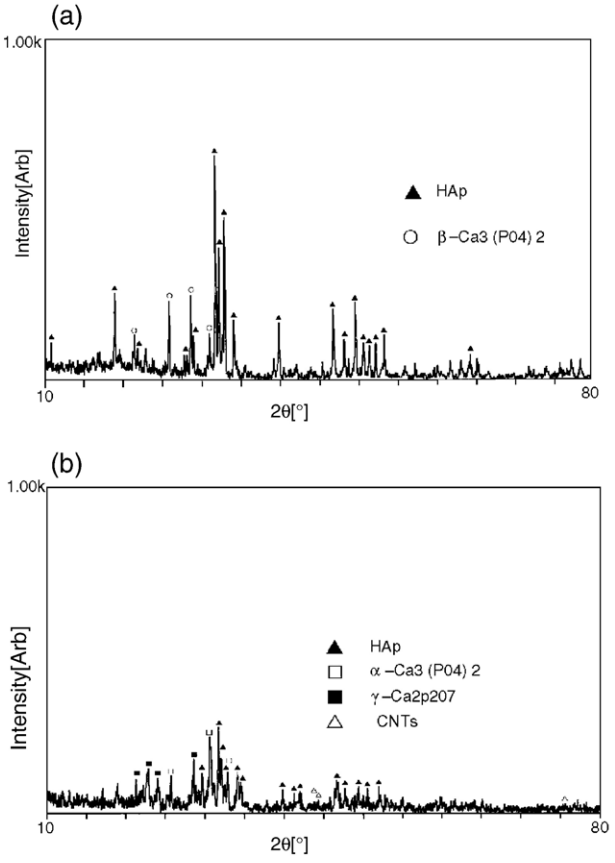

Fig. 1. The XRD pattern of HAp and MWCNTs/HAp composites after sintering. (a) pure HAp and (b) CNTs/HAp composite.

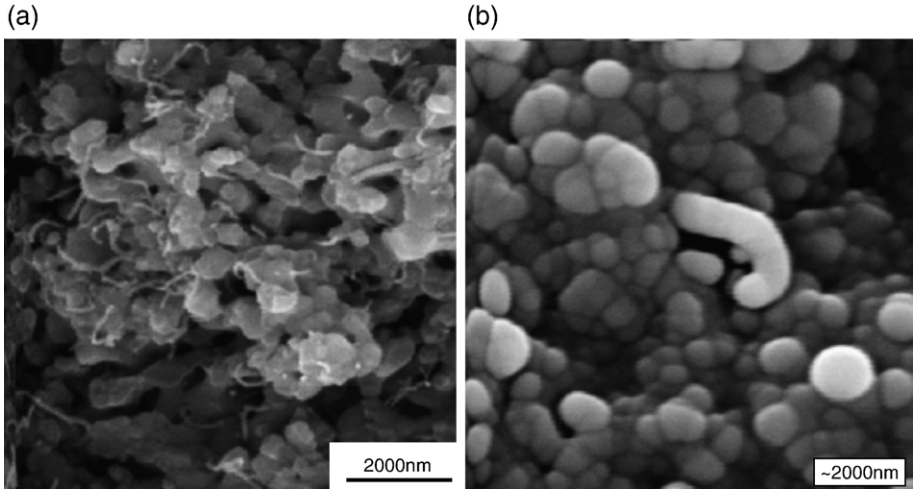

Fig. 2. The SEM micrograph of MWCNTs/HAp composite in Ar and vacuum. (a) In air and (b) in vacuum.

exceeded 100%. The fracture toughness of MWCNTs/HAp composite sintered in Ar increases by 100% and in vacuum increases by 200% compared with pure hydroxyapatite. This expressed that CNTs can strengthen and toughen hydroxyapatite. At the same time, the atmosphere can make an important effect on the mechanical properties of the composites. After analyzing we thought that MWCNTs and HAp both can absorb gas intensively, it is, therefore, in vacuum that is favorable for gas expulsion and densification of hydroxyapatite but it is contrary in Ar. The interface bonding between MWCNTs and HAp is not very strong and there is a high porosity in the composite sintered in Ar, which is in accordance with the results of the XRD pattern and SEM micrograph.

3.2. The phase composition of the MWCNTs/HAp composite

Fig. 1 exhibits the XRD pattern of pure hydroxyapatite and MWCNTs/HAp composite. Fig. 1(a) corresponds to pure hydroxyapatite and (b) corresponds to MWCNTs/HAp composite. From Fig. 1(a) we can see that most of the diffraction peaks correspond to that of hydroxyapatite (JCPDS card number: 84-1998); in addition, few diffraction peaks correspond to that of β-$Ca_3(PO_4)_2$ (JCPDS card number: 70-0316). This implies that the main crystal phase of the composites is hydroxyapatite. Since the sample was sintered in 1200 °C, this resulted to parts of hydroxyapatite decomposing and producing few β-$Ca_3(PO_4)_2$. Fig. 1(b) reveals that besides the diffraction peaks of HAp and MWCNTs there are also diffraction peaks of α-$Ca_3(PO_4)_2$ and γ-$Ca_2P_2O_7$ which indicate that hydroxyapatite decomposed further more but the main crystal phase of the composite is still hydroxyapatite. All these expressed that the addition of MWCNTs can increase the decomposition of hydroxyapatite.

3.2.1. The observation of fracture surface of MWCNTs/HAp composite with different sintering atmosphere

Fig. 2 shows the SEM micrograph of MWCNTs/HAp composite fracture surface by different sintering processes. Fig. 2(a) corresponds to MWCNTs/HAp composite sintered at 1100 °C for 3 h in Ar; Fig. 2(b) corresponds to MWCNTs/HAp composite sintered at 1100 °C for 3 h in vacuum. From (a) it could be seen that there are more residual MWCNTs in the composite than (b) and the diameter of MWCNTs does not become thicker. There are many

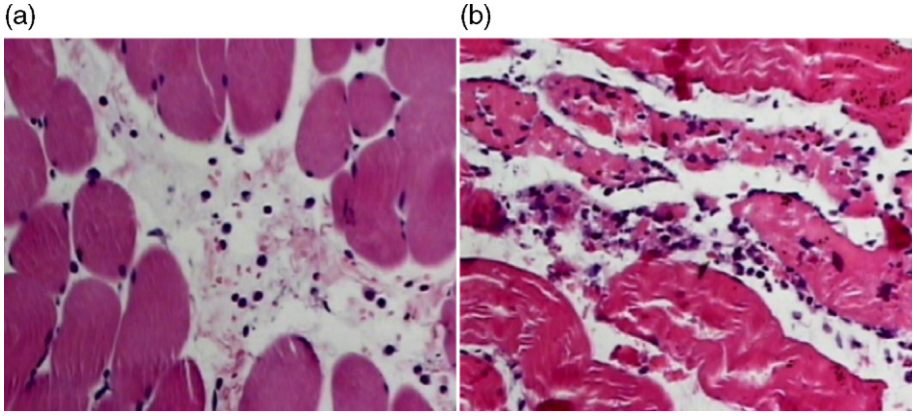

Fig. 3. The pathologic micrograph of big white mouse striated muscle after MWCNTs/HAp and ZrO_2/HAp composites were embedded for one day. (a) MWCNTs/HAp and (b) Zro_2/HAp.

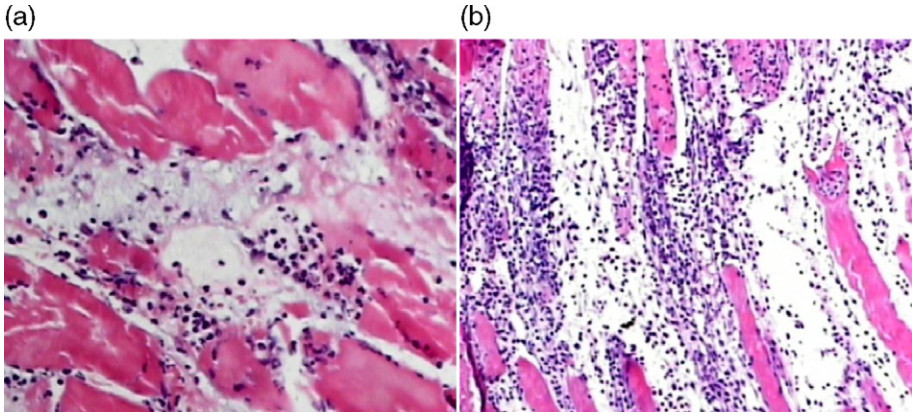

Fig. 4. The pathologic micrograph of big white mouse striated muscle after MWCNTs/HAp and ZrO_2/HAp composite were embedded for three days. (a) MWCNTs/HAp and (b) Zro_2/HAp.

pores in the composite and the interface junction between HAp and MWCNTs is not very strong. Fig. 2(b) shows that the residual content of MWCNTs in the composite sintered in vacuum is less and even produces some educts in the surface of MWCNTs. The educts grow along the surface of MWCNTs, resulting in thicker MWCNTs (the reason will be discussed in a special article). This suggests that MWCNTs can be preserved integrally in their original shape in Ar, but the interface junction between MWCNTs and HAp is loose. Although the educts grow up along the surface of MWCNTs, the interface junction between MWCNTs and HAp is strong in vacuum. Since the interface junction predominates, the mechanical properties of the composite sintered in vacuum are higher than those in Ar, which corresponds to the testing results.

4. Histocompatibility of MWCNTs/HAp biocomposite

Figs. 3, 4, 5, 6 and 7 are the histological pictures of MWCNTs/HAp and ZrO_2/HAp composite after the composites were embedded into the striped muscle for one, three, five, seven and fourteen days.

Fig. 3 is the histological pictures of MWCNTs/HAp and ZrO_2/HAp composites when they were embedded into the striped muscle for one day. Fig. 3(a) illustrates that there is little inflammatory cell and lymphocyte infiltration in the tissue around the sample and mesenchymal mild dilation hydrops. Fig. 3(b) shows that there is little inflammatory cell infiltration in the tissue around the sample but the hydrop is more serious than (a).

Fig. 4 is the histological pictures of MWCNTs/HAp and ZrO_2/HAp composites after they were embedded into the striped muscle for three days. From Fig. 4(a) we can observe that the phenomenon of inflammatory cell infiltration in the tissue around the sample is more obvious than that under one day's condition and mesenchymal moderate hydrops. Fig. 4(b) shows that there is a lot of inflammatory cell infiltration in the tissue around the sample and mesenchymal high hydrops.

Fig. 5 is the histological pictures of MWCNTs/HAp and ZrO_2/HAp composites after they were embedded into the striped muscle for five days. Fig. 5(a) exhibits that there is a lot of inflammatory cell infiltration in the tissue around the sample and the phenomenon of mesenchymal hydrops and dilation is more clear. Fig. 5(b) shows that there were many new phenomena happening in the tissue around the sample such as fibrous cell hyperplasia, blood vessel dilation, a great deal of inflammatory cell infiltration and little muscle atrophia.

Fig. 6 is the histological pictures of MWCNTs/HAp and ZrO_2/HAp composites after they were embedded into the striped

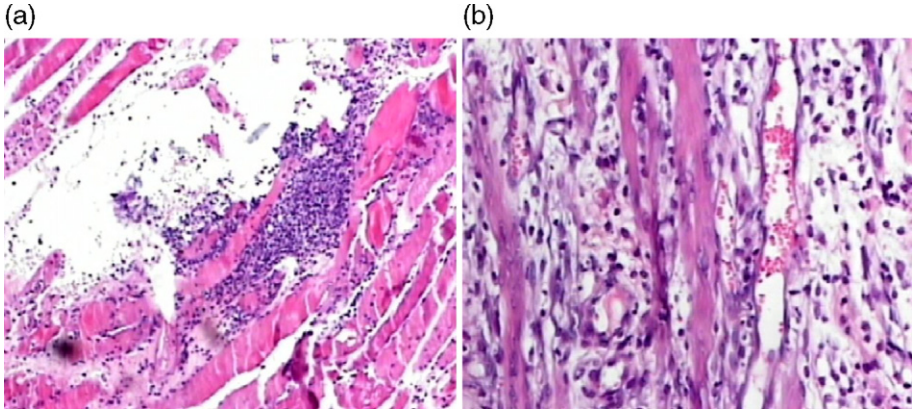

Fig. 5. The pathologic micrograph of big white mouse striated muscle after MWCNTs/HAp composite and ZrO_2/HAp composite were embedded for five days. (a) MWCNTs/HAp and (b) Zro_2/HAp.

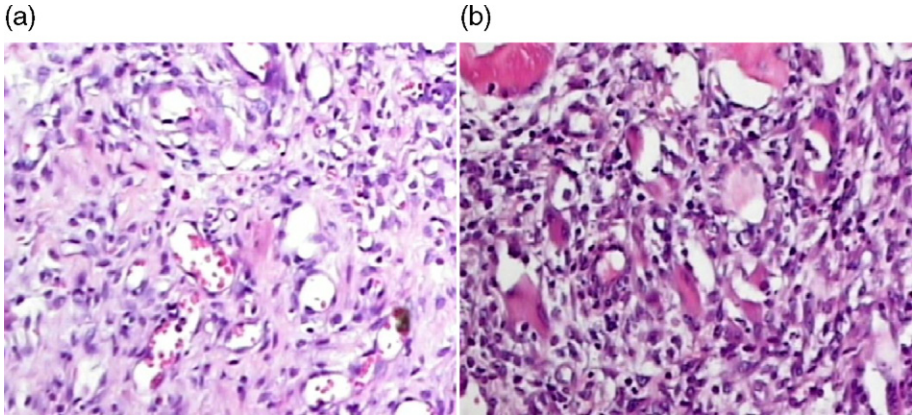

Fig. 6. The pathologic micrograph of big white mouse striated muscle after MWCNTs/HAp and ZrO_2/HAp composites were embedded for one week. (a) MWCNTs/HAp and (b) Zro_2/HAp.

muscle for seven days. As shown in Fig. 6(a), there are a lot of inflammatory cell infiltration and blood vessel dilation in the tissue around the sample. Fig. 6(b) shows that there is a lot of inflammatory cell infiltration and monocyte and foreign giant cell are produced in the tissue around the sample.

Fig. 7 is the histological pictures of MWCNTs/HAp and ZrO_2/HAp composites after they were embedded into the striped muscle for fourteen days. Fig. 7(a) illustrates that inflammatory reaction reduced and inflammatory cell infiltration decreased mesenchymal mild hydrops in the tissue around the sample. The tissue is near the natural tissue at this time. Fig. 7(b) shows that mesenchymal mild hydrops, inflammatory cell infiltration and blood vessel dilation are induced in the tissue around the sample, which implied that it has achieved the lightness time of inflammatory expression.

Through previous analysis we can see that MWCNTs/HAp and ZrO_2/HAp composites did not cause the necrosis of a mass of tissue after they were embedded into big white mouse striated muscle from one day to fourteen days. When two composites were embedded into the striated muscle for two weeks there are only little inflammatory cell and mesenchymal mild hydrops in the tissue around the composite. Meanwhile, the tissue is close to the natural tissue. This suggests that the two composites are anything but toxic. Furthermore, by comparison we find that the histocompatibility of MWCNTs/HAp composite is much better than that of ZrO_2/HAp composite.

5. Conclusions

The bending strength and fracture toughness of MWCNTs/HAp composite sintered in vacuum or Ar together with heat treatment are both higher than those of pure hydroxyapatite. The increment of the fracture toughness is most obvious and its maximum value reaches up to 2.4 MPa $m^{1/2}$, which is about eight times higher than pure HAp. MWCNTs can be preserved integrally in their original shape in Ar, but the interface junction between MWCNTs and HAp is loose and there are large numbers of pores in the composite. Although the educts grow up along the surface of MWCNTs, the interface junction between MWCNTs and HAp is strong and there are less pores in the composite in vacuum. The interface junction seems to predominate, so that the mechanical properties of MWCNTs/HAp composite sintered in vacuum are much higher than those in Ar as a whole. After MWCNTs/HAp and ZrO_2/HAp composites were embedded into big white mouse striated muscle they produced little stimulation to the tissue around the sample without arousing strictly

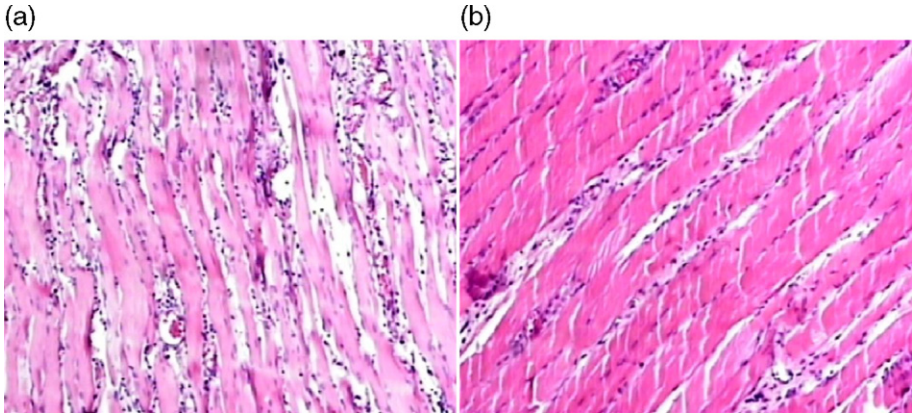

Fig. 7. The pathologic micrograph of big white mouse striated muscle after MWCNTs/HAp and ZrO_2/HAp composites were embedded for two weeks. (a) MWCNTs/HAp and (b) Zro_2/HAp.

inflammatory reaction, indicating that they are anything but toxic and possess better histocompatibility. Moreover, MWCNTs/HAp and ZrO_2/HAp composites both can satisfy the requirements of biomaterials but the histocompatibility of the former is much better than the latter.

Acknowledgments

This work was supported by the Natural Science Council (30540061) and "863" plan (2003AA302232) Republic of China.

References

[1] Dong Sheng Tang, Cheng Ming Tang, Zhao Hui Liu, et al., Journal of Shaoyang College 13 (2) (2001) 81–90.
[2] Li Jie Ci, Bing Qing Wei, Liang Ji, et al., New Carbon Material 13 (2) (1998) 65–70.
[3] T. Hayashida, L. Pan, Y. Nakayama, Physica, B 323 (2002) 352–353.
[4] Yong Liang, Ke Tao Zhan, China Powder Science and Technology 4 (4) (1998) 22–29.
[5] Jia Liang Yao, Hong Rui Peng, Zhi Kun Zhang, Journal of Qingdao Institute of Chemical Technology 23 (2) (2002) 39–42.
[6] Phaedon Avouris, Chemical Physics 281 (2002) 429–445.
[7] Wen Ping Hu, Yun Xin Liu, Peng Ju Zeng, et al., Chemical Review (2) (2000) 2–6.
[8] Hai Ning Ji, Huai Wu Zhang, Journal of Magnetic Materials Devices 32 (4) (2001) 37–40.
[9] A. Peigney, Ch. Laurent, O. Dumortier, Journal of the European Ceramic Society 18 (1998) 1995–2004.
[10] A. Peigney, Ch. Laurent, E. Flahaut, A. Rousset, Ceramics International 26 (2000) 677–683.
[11] Kin-Tak Lau, David Hui, Letters to the Editor/Carbon 40 (2002) 1597–1617.
[12] Satish Kumar, Harit Doshi, Mohan Srinivasarao, et al., Polymer 43 (2002) 1701–1703.
[13] Zhijie Jia, Zhengyuan Wang, Cailu Xu, et al., Journal of Tsinghua Univercity (Science and Technology) 40 (4) (2000) 14–16.
[14] Ai Min Li, Kang Ning Sun, Yan Sheng Yin, et al., Journal of Shandong University (Engineering Science) 33 (6) (2003) 610–615.