Effects of Surface Modification on the Dispersion Property of VGCF

FU, Yaqin^{*,a}(傅雅琴) HAN, Chunshao^a(韩春韶) NI, Qingqing^b(倪庆清)

^a Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China

^b Department of Functional Machinery & Mechanics, Shinshu University, Ueda 386-8567, Japan

In view of the easy agglomeration issue of vapor grown carbon fiber (VGCF) and the poor interfacial adhesion between VGCF and matrix resin, two-step surface modification with hydrogen peroxide and concentrated nitric acid was performed on VGCF. The surface structure and dispersion of VGCF before and after modification were tested and analyzed by XRD, TGA, FTIR, UV-visible spectrum and SEM. Moreover, VGCF/SMPU composites were prepared via a solution mixing method taking shape memory polyurethane (SMPU) as matrix, and the mechanical properties of the composites were also tested. The graphite crystal structure of VGCF showed very little change after modification, the concentration of oxygen-containing functional groups on the surface of VGCF was visibly increased, and the dispersion and dispersion stability of VGCF in organic solvent were also clearly improved. In the cross section of the VGCF/SMPU composites, the dispersion of VGCF in matrix and the VGCF-matrix interfacial adhesion observed through SEM were both enhanced to a certain extent after surface modification. The two-step surface modified VGCF had more obvious mechanical reinforcement effects on the composites than that of the pristine VGCF.

Keywords vapor grown carbon fiber, dispersion property, interfacial adhesion, two-step surface modification, oxygen-containing functional group

Introduction

Vapor grown carbon fiber (VGCF) is a fibrous product prepared from the pyrolysis of hydrocarbons in the presence of the hydrogen reductive atmosphere, catalyzed by ultra-fine particles of transition metal (Fe, Co, Ni, or their alloys).¹⁻⁷ The earliest research history of VGCF could be traced back to the end of 19th century; the first VGCF reference was a patent in 1889 owned by Hughes and Chambers, which presented "hairlike carbon filaments" from a mixture of hydrogen and methane in an iron chamber.⁸ From 1970s to 1980s, a new upsurge of VGCF research was started from the publications of $Endo^{2-4,9,10}$ in Japan and Tibbetts^{5,10} in USA. Currently, there are two typical kinds of commercial VGCF, and various dimension products from Showa Denko Inc. in Japan and Applied Sciences Inc. in USA. The unique growth mechanism of VGCF results in the formation of two different morphological partition, that is the inner ordered and layered tree ring like structure and the outside less ordered but highly graphitic chemical vapor deposition (CVD) carbon layer which is formed from the deposition of pyrolytic carbon.^{11,12} VGCF can possess many excellent properties, such as high strength, modulus, thermal conductivity,

electrical conductivity and corrosion resistance. Due to their low production cost and unique properties, VGCF can fully exert their potential as reinforcements in high performance composite materials and functional materials.¹³

The unique growth mechanism of VGCF results in a chemically inert surface, lower concentration of surface functional groups, and poor infusion with matrix materials. In addition, the strong van der Waals forces between VGCF, large aspect ratio and large specific surface area of VGCF, make them easy to agglomerate and difficult to disperse. However, surface modification can improve the concentration of surface oxygen-containing functional groups, thus enhancing the dispersion of VGCF and their interfacial adhesion with the matrix, and then VGCF can be used as an effective reinforcement to improve the mechanical properties of composites. Currently, there are relatively few publications on the surface modification of VGCF. Darmstadt studied the (12 h) oxidation of VGCF in concentrated nitric acid¹⁴ and claimed that the surface and the order of the graphitic structures in the bulk were both affected to a certain extent. Lakshminarayanan also studied the oxidation of VGCF in concentrated nitric acid.¹²

According to the above researcher's experimental

^{*} E-mail: fuyaqin@yahoo.com.cn; Tel.: 0086-0571-86843607; Fax: 0086-0571-86843250 Received November 6, 2008; revised January 12, 2009; accepted February 16, 2009. Project supported by the Program for Changjiang Scholars and Innovative Research Team in University (No. 0654), and the Key Laboratory of Ministry of Education at Zhejiang Sci-Tech University, China.

technique, a two-step surface modification was introduced on VGCF. VGCF was firstly functionalized with hydrogen peroxide and then followed by concentrated nitric acid. Hydrogen peroxide is a milder condition oxidative reagent. Li,¹⁵ Liu¹⁶ and Sung¹⁷ have studied the modification treatment of carbon nanotube (CNT) in hydrogen peroxide. They stated that various oxygen-containing functional groups such as hydroxy groups and carboxy groups, mainly the hydroxy groups would be grafted on the surface of CNT. Ros et al.¹ studied the modification treatment of carbon nanofiber (CNF) in mixtures of HNO₃/H₂SO₄ and stated that the formation of oxygen-containing functional groups occurred at defect sites on the CNF. During the oxidation process carbonyl, phenol and ether groups were formed initially, which were subsequently converted into carboxy, carboxylic anhydride and lactone groups. Therefore, a two-step surface modification is proposed to modify VGCF in this paper, to overcome the agglomeration problem through the grafting of mass oxygen-containing functional groups. Effects of surface modification on the dispersion and dispersion stability of VGCF were also studied. On this basis, shape memory polyurethane (SMPU), which possesses excellent properties and wide application potential, was selected as matrix. N-Methyl-2-pyrrolidinone (NMP), which is a good solvent for SMPU and VGCF, was selected as dispersing medium (NMP used in the experiment was just to play a role of dispersion to insure the uniform dispersion of VGCF in SMPU). VGCF/SMPU composites were prepared via a solution mixing method, and the effects of surface modification on VGCF dispersion in matrix and interfacial adhesion with matrix were also discussed.

Experimental

Materials

VGCF samples were obtained from Showa Denko Inc. in Japan with diameters of 150 nm and lengths of 10—20 µm. The matrix used in this study was shape memory polyurethane (Diary, MS4510: Diaplex Co., Ltd), supplied by Mitsubishi Heavy Industries Ltd, and its glass-transition temperature T_g was about 45 °C. The raw material was liquid, the weight ratio of polymer to solvent (DMF) was set to 3 : 7. The solvent used in this study was 1-methyl-2-pyrrolidinone (NMP, with a purity of 98%). The oxidative reagents used were hydrogen peroxide (H₂O₂) (30%, an analytical reagent), and nitric acid (HNO₃) (65%—68%, an analytical reagent).

Modification of VGCF

A two-step surface modification procedure was adopted to functionalize VGCF. The procedure was as follows:

(a) Step 1 (hydrogen peroxide)

In a typical procedure, approximately 1 of VGCF was mixed with 500 mL of 30% $H_2O_2\,\text{in}$ a round bot-

tomed flask. The mixed solution was well dispersed with the aid of ultrasonic vibration, then refluxed in an oil bath at 108 $^{\circ}$ C for 2 h. Finally, the solution was rinsed with deionized water and filtered through a 0.22 µm-pore poly(tetrafluoroethylene) membrane.

(b) Step 2 (concentrated nitric acid)

The solution from Step 1 was dispersed in 500 mL of concentrated nitric acid and refluxed in an oil bath at 115 °C for 12 h. The resulting mixture was diluted with deionized water to 2 L and then filtered through a 0.22 μ m-pore poly(tetrafluoroethylene) membrane, followed by rinsing with deionized water for several times until no residual acid was present. Then, the functionalized VGCF was dried in a vacuum oven at 100 °C for 24 h. The two-step functionalized VGCF was then stored in an airtight polyethylene bag and kept in a desiccator for further use.

Absorbance measurement of VGCF

UV-visible absorption spectrum was used to determine the dispersion property and dispersion stability of VGCF in organic solvent as follows:

(a) Choosing NMP as solvent, different concentrations of the pristine and two-step functionalized VGCF solutions were prepared by sonication (SY3100DH, 55 kHz), respectively. After adequate dispersion, the optical absorbance of VGCF at various concentrations was recorded by a computer-controlled spectrophotometer.

(b) After adequate dispersion, UV-visible absorption spectra of VGCF in NMP at the same concentration were recorded.

(c) Sedimentation experiment was conducted at a set concentration with a settled wavelength, and then, optical absorbance as a function of settling time was obtained to characterize the dispersion stability of the VGCF solution.

Measurement of the structure and surface performance of VGCF

The structure measurement of VGCF before and after modification was performed on an D8-Discover X-ray diffraction (XRD) system equipped with a position sensitive detector with a 2θ range of 120° using Cu K α (λ =1.540562 Å) radiation. The types of functional groups on the surface of VGCF were analyzed by Fourier transform infrared spectrometry (FTIR) between 1000 and 4000 cm⁻¹. The VGCF powder was milled with KBr and pressed into a tablet. The total amount of functional groups on the surface of VGCF was measured by a thermogravimetric analyzer (TGA, Pyris1). Specimens were heated from room temperature to 850 °C at a heating rate of 10 °C/min in a nitrogen flow.

Preparation of VGCF/SMPU composites and SEM observation

Firstly, the calculated amount of VGCF was dissolved in solvent and adequately wetted and dispersed. At the same time, calculated amount of SMPU was homogeneously mixed with solvent. Then the VGCF solution and SMPU solution were mixed together and homogeneously dispersed with the aid of sonication and a magnetic stirring apparatus. Finally, the mixed solution was cast into a container and dried to create VGCF/SMPU composites. In order to observe the dispersion of VGCF in the SMPU matrix, liquid nitrogen brittle fractured section of VGCF/SMPU composites was observed with scanning electron microscopy (SEM, JSM-5610LV).

Mechanical property testing of the VGCF/SMPU composites

Tensile testing was performed on various composite specimens with different VGCF weight fractions. All the samples were kept in a desiccator for 5 d prior to test. Tensile testing was conducted at room temperature [23 ± 2) °C] according to the ASTM D882-02 standard for testing on an Instron Universal Tensile tester of Instron-5543. The specimens were rectangular with approximate planar dimensions of 50 mm×10 mm. The specimen thickness was in the range of 3—3.5 mm. The initial distance between grips was 20 mm, and the tensile testing speed was 20 mm/min. Five specimens were tested for each case.

Results and discussion

XRD analysis of VGCF

The graphite crystal structure of VGCF before and after modification was studied through XRD, and the results are presented in Figure 1. Figure 1 shows that VGCF exhibits the typical structure of graphite, and the graphite crystal diffraction peaks show very little change in position, width or intensity before and after modification, indicating the graphite crystal structure has not been visibly damaged after the two-step surface modification with hydrogen peroxide and concentrated nitric acid.



Figure 1 XRD patterns of the pristine VGCF (a) and two-step functionalized VGCF (b).

FTIR analysis of VGCF

FTIR spectroscopy was used to analyze the oxygen-containing functional groups on the surface of VGCF before and after modification. The typical FTIR spectrum of VGCF before and after modification are shown in Figure 2. For the pristine VGCF, the absorption at around 1700 cm^{-1} cannot be detected, indicating there are few or no C=O groups on the surface of VGCF. An absorption peak appeared at 1720 cm⁻¹ after two-step surface modification with hydrogen peroxide and concentrated nitric acid, which has been proven to be the C=O stretching vibration of carboxy groups or carboxylic anhydride groups by many researchers.^{19,20} In addition, the absorption at about 1150 cm⁻¹ was attributed to the C—O stretching vibration,^{21,22} the weak absorption at about 1275 cm⁻¹ was attributed to the lactone groups or carbonyl groups,^{21,22} the absorption at 1384 cm⁻¹ was due to hydroxy groups,^{23,24} the absorption at 1635 cm⁻¹ was for C = C double bond groups,^{24,25} and the absorption at about 3440 cm^{-1} was for hydroxy groups.²¹ By comparing the types and absorption intensity of functional groups on the surface of VGCF before and after modification, it can be concluded that after the two-step surface modification, carboxy groups are introduced on the surface of VGCF, and the concentrations of some other oxygen-containing functional groups, such as hydroxy groups, lactone groups and ether groups appear to be strengthened, which will help to enhance the concentration of surface oxygen-containing functional groups and the dispersion of VGCF, and can be verified by TGA and UV-visible absorption spectra.



Figure 2 FTIR spectra of the pristine VGCF (a) and two-step functionalized VGCF (b).

TGA analysis of VGCF

VGCF exhibits a typical graphite structure after further heat treatment at higher temperature, and highly ordered graphite layers align along the axial direction, enabling their highly stable structure. However, since oxygen-containing functional groups are easily detached from the surface of VGCF under high temperature and cause weight loss of specimens, therefore, the concentration of oxygen-containing functional groups on the surface of VGCF can be quantitatively analyzed through the weight loss of specimens. In order to eliminate the weight loss influence of H₂O, the weight loss between

150 and 850 $^{\circ}$ C was used for further analysis.¹⁸ Figure 3 displays the TGA results of VGCF before and after modification. The solid line in Figure 3 shows that the concentration of surface functional groups of untreated VGCF is very low, and weight loss of specimen is just as low as 0.56% within the specified temperature. Combined with the FTIR results, it can be concluded that the surface functional groups of untreated VGCF are mainly hydroxy groups, which are introduced after preliminarily industrial purification. Concentration of surface functional groups of VGCF functionalized with hydrogen peroxide and concentrated nitric acid is enhanced to a large extent with weight loss amount reaching 9.7% of specimens, which is more than that of CNF functionalized with various methods in Ros's publication.¹⁸ The dashed line in Figure 3 exhibits two obvious turning points, which are sharply descending curves in about 300-400 °C and 600-700 °C. According to the weight loss characteristics of various functional groups at different temperatures summarized by Ros,¹⁸ and combined with the TGA results, it can be concluded that weight loss in about 300-400 °C is mainly losses of the introduced carboxy groups^{18,26} and hydroxy groups.²⁷ Weight loss in about 600–700 °C is mainly due to the hydroxy groups, carbonyl groups, quinone groups and ether groups, ^{18,27-29} *etc*. From the analysis of the two-stage sharply descending curves, combined with the FTIR results, it can be concluded that various oxygen-containing functional groups are introduced on the surface of VGCF and their concentration is also enhanced after the two-step surface modification. Moreover, the introduction of oxygen-containing functional groups will improve the dispersion of VGCF, which can be verified by further measurement of dispersion.



Figure 3 TGA curves of the pristine VGCF (a) and two-step functionalized VGCF (b).

Dispersion analysis of VGCF

The absorption spectra are dependent on the solution concentration in a linear fashion, following the Lambert-Beer's law.³⁰ Figure 4 is obtained by linear fitting the relationship between concentration and absorbance from experiment procedure [**Absorbance measurement of VGCF**, (a)]. The absorbance values of VGCF before

and after modification are basically adjacent at a lower concentration (20 mg/L, see Figure 4). However, with increasing concentration, the increasing absorbance rates of VGCF solution before and after modification started to show differences. The linear fitting slope of untreated VGCF is 0.0153, while the slope of functionalized VGCF is 0.01894. Difference between the two slopes indicates the different dispersion rates of VGCF in solvent before and after modification, and dispersion of VGCF is greatly improved after surface modification, especially at higher concentrations, proving the effect of modification. To further analyze the dispersion property of VGCF in solvent, the optical visible spectra were collected at concentrations of 80, 100 and 120 mg/L. Figure 5 shows the comparison of the untreated VGCF with the functionalized VGCF. The solid lines (a), (c) and (e) in Figure 5 are UV-visible spectral curves of the functionalized VGCF at concentrations of 120, 100 and 80 mg/L, respectively, and the dashed lines (b), (d) and (f) are those of the untreated VGCF at concentrations of 120, 100 and 80 mg/L, respectively. At the same concentration, a larger absorbance means better dispersion. The dispersion of functionalized VGCF is obviously improved compared with that of untreated



Figure 4 The optical absorbance (at 500 nm) of the pristine VGCF (a) and two-step functionalized VGCF (b) in NMP as a function of concentration.



Figure 5 UV-visible spectral curves of the pristine VGCF and two-step functionalized VGCF at different concentrations.

VGCF (Figure 5).

To investigate the effect of surface modification on the dispersion stability of VGCF in solvent, a sedimentation experiment procedure [Absorbance measurement of VGCF, (c)] was conducted on VGCF before and after modification at a concentration level of 100 mg/L. Within the study period, absorbance of the solution decreased in a linear fashion with time. The experiment results are shown in Figure 6. The descending slopes of the two curves are visibly different, the absorbance change rate of the untreated VGCF in solution is much faster than that of the functionalized VGCF. Resulting from the linear fitting, slope of the untreated VGCF solution absorbance as a function of time was obtained with an absolute value of 0.0278, while the absolute value of the slope of the functionalized VGCF is just 0.00772. Within the standing 22 h after dispersion, the absorbance transformation values of VGCF solution before and after modification were 0.604 and 0.168, respectively. The rate and transformation value of the untreated VGCF are 3.6 times that of the functionalized VGCF, indicating dispersion stability is significantly improved after the surface modification, as a result of the introduction of large amounts of oxygen-containing functional groups, such as carboxy groups and hydroxide groups.



Figure 6 The settling time of the pristine VGCF (a) and two-step functionalized VGCF (b) in NMP at 500 nm.

Dispersion analysis of VGCF in resin matrix

Figure 7 (a) and (b) show the image of a cross section of VGCF/SMPU composites with VGCF content of 5%, which were prepared via a solution mixing method. Obvious agglomeration of VGCF can be observed from Figure 7 (a). The chemically inert surface of the untreated VGCF, low concentration of surface oxygen-containing functional groups, poor saturation with matrix, strong van der Waals forces, large aspect ratio and large specific surface area of VGCF are all factors contributing to the agglomeration. Furthermore, some voids can also be observed in the cross section of composites, a result of both poor wettability and agglomeration. Visibly higher concentrations of surface oxygen-containing functional groups resulting from surface modification play a positive role in improving the dispersion of VGCF and the interfacial adhesion between VGCF and matrix. Dispersion of VGCF in matrix is greatly improved, agglomeration decreases, and voids are almost non-existent, indicating dispersion and interfacial adhesion with matrix are both enhanced to a certain extent after the two-step surface modification [see Figure 7 (b)]. In order to further study the interfacial adhesion between VGCF and matrix, fractured sections of composites with VGCF before and after modification obtained by applying liquid nitrogen were observed. Figure 7 (c) and (d) are the liquid nitrogen brittle fractured section of VGCF/SMPU composites with VGCF content of 10%, respectively. One can clearly observe that relatively long fibers were exposed outside the fractured section in Figure 7 (c), indicating that fibers were easily pulled out from the matrix when the composites were liquid nitrogen brittle fractured. Moreover, fibers are poorly coated by matrix. There were tiny voids at the adhesion sites of fibers and the matrix. It is obvious that, the interfacial adhesion between VGCF and matrix is poor. The exposed fibers in Figure 7 (d) are all quite shorter than those in Figure 7 (c), and more fibers are coated in matrix, mainly resulting from the various oxygen-containing functional groups introduced to the surface of VGCF after surface modification, which improved the interfacial adhesion between the fiber and matrix to a certain extent. In addition, there are no visible voids at the adhesion sites between the fibers and matrix, further illustrating the better interfacial adhesion between the VGCF and matrix after the surface modification. From these four figures one can conclude that, dispersion of VGCF in resin matrix and interfacial adhesion between the VGCF and matrix are both enhanced to a certain extent after the surface modification, which will help VGCF to play an effective role in the reinforcement of mechanical properties of composites.

Mechanical properties of the VGCF/SMPU composites

The mechanical properties of composites depend on many factors, including the amount of the filler, the degree of dispersion and the adhesion at the filler-matrix interface. In order to further substantiate the effective surface modification in the mechanical reinforcement of composites, tensile testing was performed on various composite specimens with different VGCF weight fractions. Figure 8 demonstrates the tensile and elongation at break of the VGCF/SMPU composites. Tensile strength of the composites reinforced by the two-step functionalized VGCF increases with the VGCF content, while that of the pristine VGCF reinforced composites begins to decrease after the content of 7%. When the VGCF content reaches 9%, the tensile strength of the two-step functionalized VGCF reinforced composites is increased by 66% with respect to the pure SMPU and by 36% with respect to the 9% of the pristine VGCF. In addition, it can be observed that the elongation at break



Figure 7 (a) Cross section of pristine VGCF/SMPU composites, (b) cross section of functionalized VGCF/SMPU composites, (c) fractured section of pristine VGCF/SMPU, and (d) fractured section of functionalized VGCF/SMPU.



Figure 8 Mechanical properties of VGCF/SMPU composites with various contents of the pristine VGCF and the two-step functionalized VGCF.

decreases with the VGCF content, while the two-step functionalized VGCF shows lower destruction degree on the composite elongation at break than the pristine VGCF. The above phenomenon is caused from the different dispersion of VGCF in composites and interfacial adhesion between VGCF and SMPU. Therefore, the two-step functionalized VGCF shows much better mechanical reinforcement on the composites than the pristine VGCF, which again is a result that provides evidence of the benefic effects of the two-step surface modification of the VGCF in the preparation of the VGCF/SMPU composites.

Conclusion

Two-step surface modification of VGCF was performed with hydrogen peroxide and concentrated nitric acid, and the surface structure, dispersion and dispersion stability of VGCF before and after modification were investigated. On this basis, VGCF/SMPU composites were prepared via a solution mixing method, and the dispersion of VGCF in matrix and VGCF-matrix interfacial adhesion were also observed. The mechanical properties of the composites were also tested. The results obtained are concluded as follows:

(a) After surface modification with hydrogen peroxide and concentrated nitric acid, the graphite crystal structure of VGCF is hardly transformed, while a large number of various oxygen-containing functional groups are introduced onto the surface of VGCF.

(b) Both the dispersion and dispersion stability of VGCF in solvent after surface modification are improved to a large extent compared with the pristine VGCF.

(c) In the VGCF/SMPU composites prepared via a solution mixing method, the dispersion and interfacial adhesion of VGCF in resin matrix are improved to a certain extent after surface modification, which will be beneficial to VGCF effective reinforcement of the mechanical properties of composites.

(d) According to the mechanical property testing, the two-step functionalized VGCF shows much better mechanical reinforcement on the composites than the pristine VGCF.

Acknowledgements

The authors wish to thank the testing assistance of the instrumental Analyse Center of Zhejiang Sci-Tech University.

References

1 He, F. *Carbon Fiber and Its Application Technology*, Chemical Industry Press, Beijing, **2004**, p. 189 (in Chinese).

- 2 Koyama, T.; Endo, M. Jpn. J. Appl. Phys. 1974, 13, 1175.
- 3 Oberlin, A.; Endo, M. J. Cryst. Growth 1976, 32, 335.
- 4 Endo, M. Chem. Tech. 1988, 18, 568.
- 5 Tibbetts, G. G. Carbon 1989, 27, 745.
- 6 Gupta, S. K.; Gupta, N.; Kunzu, D. J. Anal. Appl. Pyrolysis 1993, 26, 131.
- Darmstadt, H.; Roy, C.; Kallaguine, S.; Ting, J.-M.; Alig, R.
 L. *Carbon* 1998, *36*, 1183.
- 8 Hughes, T. V.; Chambers, C. R. US Patent 405, 1889.
- 9 Koyama, T.; Endo, M. Buturi Oyo 1973, 42, 690.
- Tibbetts, G. G.; Endo, M.; Beetz, C. P. SAMPE J. 1986, 22, 30.
- Madronńero, A.; Ariza, E.; Verdu, M.; Brandl, W.; Barba, C. J. Mater. Sci. 1996, 31, 6189.
- Lakshminarayanan, P. V.; Toghiani, H.; Pittman Charles, J. U. *Carbon* 2004, *42*, 2433.
- 13 Chen, X. H.; Shen, Z. M. Carbon Tech. 1999, 104, 18 (in Chinese).
- 14 Darmstadt, H.; Summchen, L.; Ting, J.-M.; Roland, U.; Kaliaguine, S.; Roy, C. *Carbon* **1997**, *35*, 1581.
- 15 Li, C. C.; Lin, J. L.; Huang, S. J.; Lee, J. T.; Chen, C. H. Colloids Surf., A: Physicochem. Eng. Aspects 2007, 297, 275.
- 16 Liu, M. H.; Yang, Y. L.; Zhu, T.; Zhong, F. L. Carbon 2005, 43, 1470.
- 17 Sung, Y. T.; Han, M. S.; Song, K. H.; Jung, J. W.; Lee, H.

S.; Kum, C. K.; Joo, J.; Kim, W. N. Polymer 2006, 47, 4434.

- 18 Ros, T. G.; Van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. *Chem. Eur. J.* **2002**, *8*, 1151.
- 19 Jian, C.; Hamon, M. A.; Hui, H.; Yongsheng, C.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. Science **1998**, 282, 95.
- 20 Liu, Y. X.; Du, Z. J.; Li, Y.; Zhang, C.; Li, H. Q. Chin. J. Chem. 2006, 24, 563.
- 21 Zielke, U.; Hüttinger, K. J.; Hoffman, W. P. *Carbon* **1996**, *34*, 983.
- 22 Song, H. J.; Zhang, Z. Z.; Men, X. H. Eur. Polym. J. 2007, 43, 4092.
- 23 Ma, P. C.; Kim, J. K.; Tang, B. Z. Carbon 2006, 44, 3232.
- 24 Kathi, J.; Rhee, K. Y. J. Mater. Sci. 2008, 43, 33.
- 25 Chen, Y. H.; Lin, A.; Gan, F. X. Appl. Surf. Sci. 2006, 252, 8635.
- 26 Aksoylu, A. E.; Madalena, M.; Freitas, A.; Pereira, M. F. R.; Figueiredo, J. L. *Carbon* 2001, *39*, 175.
- 27 Kazuhisa, M.; Tetsuo, M. Langmuir 1994, 10, 807.
- 28 Moreno-Castilla, C.; Ferro-García, M. A.; Joly, J. P. Bautista-Toledo, I. *Langumir* 1995, 11, 4386.
- 29 Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Orfao, J. J. M. *Carbon* **1999**, *37*, 1379.
- 30 Qin, Y. J.; Liu, L. Q.; Shi, J. H.; Wu, W.; Zhang, J.; Guo, Z. X.; Li, Y. F.; Zhu, D. B. Chem. Mater. 2003, 15, 3256.

(E0811061 Pan, B.; Lu, Z.)