Growth and characterization of BCN nanotubes with high boron and nitrogen content

GUO ZHANG, ZHIYE LIU, LIANPING ZHANG, LIQIANG JING and KEYING SHI*

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Key Laboratory of Material Chemistry, School of Chemistry and Chemical Engineering, Heilongjiang University, Harbin 150080, People's Republic of China
e-mail: shikeying2008@yahoo.cn

MS received 12 August 2012; revised 4 January 2013; accepted 2 August 2013

Abstract. Multiwalled carbon nanotubes doped with boron and nitrogen (BCNTs) have been synthesized by chemical vapour deposition at temperatures ranging from 800°C to 950°C. Their morphological and structural features have been studied by transmission electron microscope, which reveal that BCNTs have bamboo-like structure. The results of X-ray photoelectron spectroscopy demonstrated that the atomic ratio of B, C and N of BCNTs is about 1:4:1, when temperature is 850°C. Electrooxidation performance of the BCNTs for NO at the modified electrodes was investigated. The results of cyclic voltammograms and the electrochemical impedance spectroscopy of BCNT-modified electrodes indicated that the activity of NO electrooxidation on 850°C-modified electrodes is much stronger than others and the charge transfer resistance of NO electrooxidation BCNT-modified electrode is the least. By this means, BCNT-modified electrodes showed excellent electrode materials for NO detection and other potential applications.

Keywords. Chemical vapour deposition (CVD); boron carbide nitride nanotubes (BCNTs); BCNT-modified electrode; NO electrooxidation.

1. Introduction

Carbon nanotubes (CNTs) have evoked considerable research interest owing to their remarkable electronic, mechanical, and optical properties.^{1,2} The unique properties of CNTs gave enormous impetus to researchers to explore analogous materials, such as boron nitride nanotubes (BNNTs), boron carbide nitride nanotubes (BCNTs). Thereinto, BNNTs are semiconductors characterized by wide band-gap energy of about 5.5 eV, independent of their radius and helicities.³ It is noteworthy that BCNTs are interesting in their own right and maybe able to offer different possibilities for technological applications that CNTs and BNNTs cannot provide.⁴ As ternary B–C–N materials, BCNTs are fascinating semiconductors with a ‘tunable’ band gap energy that is primarily controlled by the structure and chemical composition.⁵ It has also been found that BCNTs obtained by partial substituting of C for B or N would alter the hardness and electronic properties.⁶

Compared to carbon nanotubes, BCNTs have some advantageous properties such as semiconductive,⁷ mechanical,⁸ being having good electrical performance and higher resistance to oxygen.⁹ All these properties provide BCNTs great potential for application in electronics,¹⁰ optoelectronics,¹¹ high temperature lubricants¹² and other applications.¹³ Especially in nano-electrochemistry, it provides the possibility to produce materials with tunable electronic properties. Therefore, as one of the important B–C–N materials, BCNTs have been intensively studied theoretically and experimentally.^{14–16} BCNNTs are particularly useful in nanodevice applications where high-strength and semiconductor properties are desired. In terms of their structural stability, theoretical calculations predict that segregation of the BN, C, and BCN domains tends to occur; the most stable structure seems to optimize the chemical bond energy by maximizing the number of C–C and B–N bonds. Their structure and composition appear to be sensitive to the growth method and actual growth parameters. Therefore, systematic studies of the characteristics of BCNTs grown using specific techniques are of great importance both to further their utilization and to develop suitable fabrication methods.

*For correspondence

In recent years, several synthesis techniques have been developed for growth of BCNTs, including arc discharge,¹⁶ laser ablation,¹⁷ pyrolysis¹⁸ and chemical vapour deposition (CVD).¹⁹ However, most of these synthesis methods were carried out at high temperatures.²⁰ Kim *et al.*¹⁶ synthesized BCNTs using BN power, iron phthalocyanine and NH_3 as B, C, N source at 1200°C . Wu *et al.*²² synthesized BCN nanotubes with CVD derived using carbon NTs together with B_2O_3 and N_2 at 1600°C for half an hour. It was found that the new trend of low temperature synthesis was necessary. Thus, to develop a low-temperature, high-quality synthesis method for BCNTs with a higher production yield is the highest priority for their practical application.

At present, NO is an active molecule with short half-life, low concentration, low stability, high reactivity and other very active free radicals present in the environment.²³ Electrocatalytic properties for NO electrooxidation have also been investigated based on the modified electrodes with carbon nanotubes and analogous carbon nanotube structure.²⁴ We expect to establish a highly sensitive method to detect NO in aqueous solution with BCNTs. Thus, preparing BCNTs and investigating their NO electrooxidation property are very meaningful.

In the present study, we report on the direct, large-scale synthesis of ternary BCNNTs, which carried out a simple growth method by using ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) solution of borohydride (NaBH_4) and dicyclopentadienyl iron as source material. Through the change of reaction temperature, four different types of multiwalled BCNNTs (different atomic ratios of B:C:N) are prepared. All the processes have been simple and low cost. This approach makes it possible to control the morphology, and the chemical composition of BCNNTs could be tailored by varying reaction temperature. Moreover, the electrocatalytic properties for NO electrooxidation have also been investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1 Material preparation

BCNTs were synthesized via CVD, which was carried out in a horizontal reactor consisting of a quartz tube. NaBH_4 was used as boron precursor, $\text{Fe}[\text{C}_5\text{H}_5]_2$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ were chosen as carbon and nitrogen sources. We used froth iron powder as a catalyst precursor and placed it in a quartz boat in a system, which is composed of an electrical furnace internally

equipped with a quartz tube. One end of the quartz tube is connected to a wide-mouth bottle filled with the source solution. First, nitrogen gas was introduced into the sample quartz tube to remove oxygen adsorbed on the surface. Then, H_2 was introduced into the system to reduce the catalyst at reaction temperature for 30 min. Subsequently, B, C, N sources were introduced into the reactor with N_2 as carrier gas, and the reaction was maintained at different reaction temperatures (800°C – 950°C) for 1 h. After cooling down to room temperature in a flow of N_2 , the products were collected.

2.2 Electrochemical experiments

Glassy carbon (GC) electrode with diameter of 4 mm was polished before each experiment, then sonicated in ethanol, acetone and water, respectively and dried at ambient temperature. The BCNNTs synthesized at different temperature were used to modify the GC electrode. Each BCNNTs of quantity 0.25 mg was dispersed in 10 mL acetone accompanied by ultrasonic process to get a suspension. Suspension of $10\ \mu\text{L}$ was dropped on the surface of the GC electrode, and the solvent was gradually evaporated under an IR lamp. Then three kinds of modified electrodes were obtained. Electrochemical experiments were performed in an electrolytic cell with three electrodes. The GC electrode or various SWCNT-modified electrodes were used as a working electrode, a platinum sheet served as an auxiliary electrode, and an Ag/AgCl electrode was used as a reference electrode. KH_2PO_4 – NaOH buffer solution (PBS) of $0.1\ \text{mol L}^{-1}$ was taken as a blank solution, the pH value was 6.8. The solution was bubbled by high purity N_2 (99.999%), for 30 min to remove oxygen, and then the solution was bubbled with pure NO (99.999%) for 30 min to prepare a NO-saturated solution. The CV was measured by LK98IIB electrochemical analyser (Lanlik Instrument Co. Ltd., Tianjin, China), the scanning speed was $50\ \text{mV s}^{-1}$, and the range of potential sweep was 300–1400 mV. The EIS was measured by IM6e impedance measurement unit (ZAHNER Elektrik, Germany). The AC voltage amplitude was 10 mV, the frequency range was from 10 mHz to 100 kHz, and the data were processed with Zview2 software.

2.3 Material characterization

The morphology and structure of the products were studied using transmission electron microscopy (TEM, JEM-2100). C, N and B elements were quantified by

X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) excited by an X-ray source of Mg K α ($h\nu < 1253.6$ eV) in an ultrahigh vacuum chamber with a base pressure of $<2 \times 10^{-8}$ Torr. The Fourier transform infrared (FT-IR) spectra were carried out with FTIR Spectrometer (Perkin Elmer Spectrum). Cyclic voltammetry (CV) measurements were performed by BAS100B electrochemical analyser (Germany). The experiments were carried out at 0.05 V s^{-1} . A conventional three-electrode configuration was used with a GC modified electrode as working electrode, an Ag/AgCl electrode (in KCl saturated solution) as reference electrode, and a platinum sheet as counter electrode. The prepared BCNTs were dropped onto a modified glass carbon to measure their NO electro-oxidation performance.

3. Results and discussion

Figure 1 presents TEM images of BCNTs synthesized by CVD method at temperatures ranging from (800°C – 950°C). Figure 1(a–c) shows the low and high magnification TEM images of BCNTs synthesized at 800°C . Figure 1(a, b) reveal that BCNTs possess curved intersecting inner wall. In fact, figure 1(c) illustrates a tubular structure with opened edges, and the diameter of BCNTs is about 30–50 nm. It is notable that these nanofibres have been produced only at 800°C . Figure 1(d–f) are the TEM images of BCNTs synthesized at 850°C . It can be observed that the BCNTs are composed of many curved graphite layers (figure 1e, f). It is the curved graphite layers that make up the stacked ‘bamboo-like’ compartments. The diameter

Figure 1. TEM images of BCNTs obtained by different synthesis temperatures: (a), (b), (c) 800°C ; (d), (e), (f) 850°C ; (g) 900°C ; (h) 950°C .

of BCNT is about 60 nm. High-resolution transmission electron microscopy (HRTEM) image clearly shows that the BCNT are multiwalled and have bamboo-like structure with a very frequent and regular compartmentalized morphology which is a typical result of doped heteroatoms. Figure 1(g) shows that the distorted structural BCNTs synthesized at 900°C result in bending and curling, the bamboo-like structure is irregular. Figure 1(h) shows that BCNTs synthesized at 950°C are of pell-mell structure, the compartment layers are curved to connect with the distorted wall. The above result suggests that BCNT growth and atom rearrangement occur at the crush edges due to their high temperature. In addition, it should be noted that the growth of the BCNTs progresses outwards with an increase in the diameter as further layers are added during the formation.²⁵ Results demonstrate that temperature had a great effect on the morphology of the BCNTs, and the best synthesized temperature of BCNTs is 850°C.

Figure 2 shows typical infrared absorption spectra of the sample groups of BCNTs grown at various temperatures. Figure 2(a–d) shows two bands around 1386 cm^{-1} and 795 cm^{-1} , corresponding to in-plane B–N transverse optical mode²⁶ and out-of-plane B–N–B bending mode of BCNTs.²⁷ A very wide absorption band at around 1020–1220 cm^{-1} is observed.²⁸ The absorption bands at 1045 cm^{-1} and 1125 cm^{-1} were due to C–N and C–B²⁹ bending vibration, respectively. The absorption band at 1631 cm^{-1} is assigned to the presence of sp^2 -bonded C=N bond.^{30,31} In addition, the absorption band centred at 3445 cm^{-1} is related to N–H or O–H stretching vibrations or water molecules.³² The FT-IR spectra confirm that the B and N atoms have been doped into the BCNTs.

The chemical states of B, C, and N elements were investigated using X-ray photoelectron spectroscopy

(XPS) spectra. The chemical composition of the as-prepared BCNTs is exhibited in table 1. According to the results of the XPS, BCNTs have the highest doped B and N at 850°C. The chemical states of B, C, and N elements of the sample under 850°C are further researched. Since it is important for the N element in different samples to adsorb NO, the four samples of chemical states of N have been investigated. It is noted that the atomic ratio of B, C and N of BCNTs synthesized by 850°C is close to 1:4:1. To further investigate the local structure of the as-obtained materials, the 1s peaks of N, C, B and O are revealed, respectively, in figure 3(a), and these peaks are separated by Gaussian fitting. As shown in figure 3(b), the spectrum is mainly composed of two peaks through Gaussian fitting. The peak of N1s with binding energies of 398.2 eV can be assigned to the N atoms in pyridine-like N–C structures;^{33–35} the peak of N1s with binding energies of 399.0 eV can be assigned to the N atoms bonded to C atoms as graphite-like structures.^{11,35} The sp^2 -bonded B=N and C=N bonds are known to emit photoelectrons that bonded to the core state of N at 398.0–398.3 eV and 399–400 eV, respectively.^{33–35} The content of pyridine-like N in the sample at 850°C is highest among the four samples. Similarly, the C1s spectrum in figure 3(c) has three peaks with a broad shoulder. The curve-fitted C 1s spectrum shows three main peaks centred at 284.5, 285.2 and 286, which are ascribed to sp^2 C=B, C=C and C=N, respectively.^{36–38} The presence of negligible C=O bonding structures located at 289.4 eV are due to surface contaminant oxidized dangling bonds at the defect sites of tube walls. The B 1s spectrum in figure 3(d) indicates that there are two bonding states. The peak at 190.5 eV corresponds to boron bonded to carbon (B–C bond), the peak at 191.2 eV is assigned to boron bonded to nitrogen (B=N bond).¹⁶ This spectrum indicates that most B are bonded to N in the form of sp^2 bonded B=N bonds, the results suggest that the boron and nitrogen bonding exists in the structure of as-grown nanotubes.

Figure 4 represents the schematic procedure of the preparation of BCNNTs composites under different growth steps. It is clear that catalyst particle BCNNTs were catalytically synthesized with C and N resources

Figure 2. FT-IR spectra of BCNTs prepared at different temperatures: (a) 800°C, (b) 850°C, (c) 900°C and (d) 950°C.

Table 1. Total elements concentration (at.%) of BCNTs at different temperature.

Sample	O1s %	N1s %	C1s %	B1s %
800°C	6.46	9.77	77.35	6.43
850°C	8.05	14.88	62.01	15.07
900°C	5.46	13.03	69.74	11.77
950°C	6.11	7.76	79.21	6.91

Figure 3. XPS spectrum of BCNTs synthesized at 850°C: (a) 1s peaks of N, C, B, and O; (b) N 1s; (c) C 1s and (d) B 1s peaks separated by Gaussian fitting.

over Fe–Mg catalyst and the reaction temperature was optimized for the first step. At reaction temperature, carbon atoms that also originate from the pyrolysis of C and N resources start reacting on the hot metal catalyst clusters, and thus the N-doped carbon multiwall part is first synthesized, N can be doped as pyridine-like N structures or as graphite-like N structures. The C atoms found around N atoms as graphite-like structures are active because N atoms are modified. In the second stage of synthesis, the chemical vapour deposition (CVD) process gives rise to a B-doped carbon layer on the already-deposited N-doped carbon multiwall.

The B atoms replace the C atoms around the N atoms as graphite-like structures or occupy the centre of the pyridine-like N, leading to the formation of BCNNTs.

Figure 5 shows the result of CVs at various temperatures BCNT-modified electrodes in 0.1 M phosphate buffer solution (PBS, pH 6.8) saturated with NO. CV studies were performed within the potential range of 0.3 to 1.4 V. The values of peak current density and peak potential of BCNTs synthesized at 800°C, 850°C, 900°C, 950°C at modified electrodes are shown in table 2. The peak current reflects the rate of the electrode reaction, and the peak potential reflects the

Figure 4. Schematic diagram of the fabrication of BCNNTs.

Figure 5. Cyclic voltammograms at (a) 850°C, (b) 900°C, (c) 800°C and (d) 950°C BCNT-modified electrodes in PBS saturated with NO (scan rate of 50 mV/s).

activation energy of the electrode reaction. In general, the higher the peak current density, the faster the reaction rate of NO electrooxidation.³⁹ It can be seen that BCNT-modified electrode synthesized at 850°C has the highest current density and the one with most negative peak potentials. The anodic peak potential is 0.822 V and the peak current density is 23.53 mA/cm². Meanwhile, the order of NO electrooxidation rate of various BCNT-modified electrodes is BCNT-850°C > BCNT-900°C > BCNT-800°C > BCNT-950°C. Thus, the rate of NO electrooxidation of BCNT-850°C modified electrode is the highest among all the BCNT-modified electrodes. This result is attributed to increased boron–nitrogen doping of BCNT leading to increased defects and improved activity on BCNT surface. Figure 3(b) and table 1 reveal the XPS N 1s spectra and N content of the samples, the order of concentration of N atom in nanotubes is BCNT-850°C > BCNT-900°C > BCNT-800°C > BCNT-950°C among the four BCNTs.

Table 2. The values of peak potential, current density and charge transfer resistance (R_{ct}) for NO electrooxidation.

Modified electrode	NO electrooxidation peak		R _{ct} (Ω)
	Potential (V)	Current density (mA/cm ²)	
800°C	0.839	16.71	381
850°C	0.822	23.53	315
900°C	0.815	17.61	352
950°C	0.838	13.76	418

It can be speculated that N content in BCNTs is important for electrocatalysis capability. Therefore, electrocatalysis capability increases with nitrogen content in BCNTs synthesized under different temperatures. The XPS N 1s spectra are mainly composed of two peaks through Gaussian fitting (figure 3b). The 398.2 eV peak can be assigned to N atoms in the pyridine-like N–C structures, the 399 eV peak can be assigned to the N atoms bonded to C atoms as graphite-like structures. Either pyridine-like N or graphite-like N is important to adsorb NO and favour NO catalytic oxidation.⁴⁰ Therefore, the increase of N element in BCNTs is benefit for the NO catalytic oxidation. In addition, in four samples, the BCNTs are uniform and the atomic ratio of B, C and N of BCNTs synthesized at 850°C is close to 1:4:1. The concentration of B and N atoms in nanotubes is highest among the four BCNTs. In addition, it can be seen in figure 3(b) that the sample which was prepared at 850°C contains a large amount of the pyridine-like N. Pyridine-like N is very important because of the extra lone pair of electrons on the N atom, which increases electron density on graphitic edge planes. Therefore, it is reasonable to expect that edge planes, which are commonly known to be reactive sites for the oxidation of NO, will show increased reactivity due to electron density garnered from the incorporation of N in pyridine-like coordination.^{40,41} Therefore, BCNT-850°C reflects higher electrocatalytic activity.

Electrochemical impedance spectroscopy (EIS) is a powerful tool which can provide a wealth of information for electrode reactions. We employed EIS to further investigate the activity of these two electrodes towards PBS saturated with NO solution electrooxidation. For comparison, figure 6 presents the Nyquist plots of BCNT-modified electrodes measured in PBS saturated with NO solution at a potential of 0.60 V. An AC voltage amplitude of 0.01 V was used in the frequency range of 1 Hz to 100 kHz. Resistance can be obtained from the analysis of EIS spectra by using Z-view software. Diameter of the capacitive semicircle which represents the resistance of charge transfer decreases when the electrode potential is 0.6 V. As shown in figure 6 and table 2, there are big capacitive semicircles of BCNTs synthesized at 950°C and BCNT-modified electrodes synthesized at 850°C are small. The change in capacitive semicircles occurs due to the influence of the products charge transfer resistance. The value of charge transfer resistance (R_{ct}) of BCNT-modified electrodes synthesized at 800°C, 850°C, 900°C and 950°C are shown in table 2. It is known that the lower R_{ct} of the modified electrode corresponds to the faster rate of charge transfer. The order of charge transfer rate is BCNT-850°C > BCNT-900°C > BCNT-800°C >

Figure 6. Nyquist plot of electrochemical impedance spectroscopy of (a) 850°C, (b) 900°C, (c) 800°C and (d) 950°C BCNTs.

BCNT-950°C. It shows that the diameter of capacitive semicircle increases with increase in electrode potential.

4. Conclusion

Our study discusses the structure and properties of carbon doped with nitrogen and boron via CVD procedure in the temperature ranges 800°C–950°C. TEM indicates that the BCNTs at 850°C usually have a perfect bamboo-like structure. XPS data of BCNT-850°C reveal that the B, C and N atomic ratio is nearly 1:4:1. This reveals significant binding states of B=N and C=N. Electrocatalytic properties of BCNTs have been investigated by CV in 0.1 M PBS at room temperature. Corresponding results show that BCNT-850°C can be taken as an optimal electrode material. The sensitivity of BCNT-850°C-modified electrode is the highest of all experimental electrodes. The Rct of NO electrooxidation BCNT-850°C-modified electrode is the least. Therefore, BCNT-850°C can be taken as an optimal electrode material. The sensitivity of BCNT-850°C-modified electrode is the highest of all experimental electrodes. This suggests that BCNT-based electrodes have potential electronic applications.

Acknowledgement

This work was supported by the Union Funds of Scientific Research Fund of Heilongjiang Provincial Education Department (No. 12521421).

References

1. Dominik E 2010 *Chem. Rev.* **110** 1348
2. Abhishek K K, Erkan K and Brian W S 2009 *J. Mater. Sci.* **44** 6020
3. Renzhi M, Yoshio B and Tadao S 2002 *Adv. Mater.* **14** 5
4. Yu J and Bai X D 2000 *Chem. Phys. Lett.* **323** 529
5. Su C Y, Juang Z Y and Chen K F 2009 *J. Phys. Chem. C* **113** 14681
6. Pattanayak J, Kar T and Scheiner S 2002 *J. Phys. Chem. A* **106** 2970
7. Lei W W, Portehault D and Dimova R 2011 *J. Am. Chem. Soc.* **133** 7121
8. Golberg D, Costa P and Lourie O 2007 *Nano Lett.* **7** 2146
9. Yin L W, Bando Y and Golberg D 2005 *J. Am. Chem. Soc.* **127** 16354
10. Yang X X, Liu L and Wu M H 2011 *J. Am. Chem. Soc.* **133** 13216
11. Terrones M, Grobert N and Terrones H 2002 *Carbon* **40** 1665
12. Raidongia K, Jagadeesan D and Mousumi U K 2008 *J. Mater. Chem.* **18** 83
13. Wang W L, Bai X D, Liu K H and Xu Z 2006 *J. Am. Chem. Soc.* **128** 6530
14. Bhattacharya S, Majumder C and Das G P 2009 *J. Phys. Chem. C* **113** 15783
15. Matos M A, Azevedoa S and Kaschny J R 2009 *Solid State Commun.* **149** 222
16. Kim S Y, Park J and Choi H C 2007 *J. Am. Chem. Soc.* **129** 1705
17. Terrones M, Golberg D, Grobert N, Seeger T, Reyes-Reyes M, Mayne R, Kamalakaran R, Dorozhkin P, Dong Z C, Terrones H, Ruhle M and Bando Y 2003 *Adv. Mater.* **15** 1899
18. Dominick V, Lanzisera and Andrews L 1997 *J. Phys. Chem. A* **101** 7134
19. Sen R, Satishkumar B C, Govindaraj A and Harikumar K R 1998 *Chem. Phys. Lett.* **287** 671
20. Stéphan O, Ajayan P M, Colliex C and Redlich Ph 1994 *Science* **266** 1683
21. Ma R and Bando Y 2002 *Chem. Mater.* **14** 4403
22. Wu J, Han W Q, Walukiewicz W, Ager J W III, Shan W, Haller E E and Zettl A 2004 *Nano Lett.* **4** 647
23. Xu X, Yang L J and Jiang S J 2011 *Chem. Commun.* **47** 7137
24. Dong J P, Qu X M and Wang L J 2008 *Electroanalysis* **18** 1981
25. Pokropivny V V, Shorokod V V and Oleinik G S 2000 *J. Solid State Chem.* **154** 214
26. Gao R, Yin L W and Wang C X 2009 *J. Phys. Chem. C* **113** 15160
27. Caretti I, Jim J and Albella J M 2003 *Diam. Relat. Mater.* **12** 1079
28. Kim D H, Byon E and Lee S 2004 *Thin Solid Films* **447–448** 192
29. Zhou Z F, Bello I and Lei M K 2000 *Surf. Coatings Technol.* **128–129** 334
30. Yap Y K, Kida S and Aoyama T 1998 *Appl. Phys. Lett.* **73** 915
31. Yap Y K, Kida S, Wada Y, Yoshimura M and Mori Y 2000 *Diam. Relat. Mater.* **9** 1228

32. Kan K, Xia T L, Li L and Bi H M 2009 *Nanotechnology* **20** 185502
33. Berns D H and Cappelli A 1996 *Appl. Phys. Lett.* **68** 2711
34. Zhang T, Wen G W and Huang X X 2010 *Cryst. Eng. Commun.* **12** 3506
35. Chen Y, Zou J and Campbell S J 2004 *Appl. Phys. Lett.* **84** 2430
36. Linss V, Rodilb S, Reinkec P and Garnierd M 2004 *Thin Solid Films* **467** 76.
37. Mannan M A, Nagano M and Kida T 2009 *J. Phys. Chem. Solids* **70** 20
38. Tamikuni K 2004 *J. Mater. Chem.* **14** 221
39. Zhang R, Li L and Chen L 2011 *J. Alloys Compd.* **509** 8620
40. Lv W X, Zhang R, Xia T L, Bi H M and Shi K Y 2011 *J. Nanopart. Res.* **13** 2351
41. Maldonado S, Morin S and Stevenson K J 2006 *Carbon* **44** 1429