

A scalable CVD synthesis of high-purity single-walled carbon nanotubes with porous MgO as support material

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The choice of support and catalyst materials has been proved to be critical to scalable chemical vapor deposition (CVD) synthesis of carbon nanotubes. In our study, we found that porous MgO prepared by thermal decomposition of its salts was an eminent support material for CVD growth of single-walled carbon nanotubes (SWNTs). Compared with other kinds of supports such as SiO₂, ZrO₂, Al₂O₃ and CaO *etc.*, the quality of as-grown SWNTs on MgO supports was stable; the effects of reaction conditions such as furnace temperature, flow rate of the gas and the types of catalysts and supports on the properties of as-prepared SWNT products were thoroughly investigated and characterized by micro-Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetry (TG) techniques. The results indicated that the yields of SWNTs on MgO supports could be up to about 120% with the addition of a small amount of assistant catalyst Mo salt. The obtained purity of the as-grown products was higher than 90% after treatment with 4 M HCl. The obvious advantages of using MgO supports include efficient and stable growth of SWNTs, scalable synthesis of SWNTs at low cost, and easy removal of the support in mild acid, causing little harm to the products.

1 Introduction

Carbon nanotube materials are now regarded as promising materials owing to their unique chemical and physical properties and great potential applications. Since multi-walled carbon nanotubes (MWNTs) were first synthesized in 1991,¹ and single-walled carbon nanotubes (SWNTs) in 1993,² numerous attempts have been made to synthesize such products on a large-scale and at low-cost. Until now, carbon nanotubes have been synthesized by arc-discharges,³ laser ablation,⁴ catalytic chemical vapor decomposition (CVD),⁵ flame synthesis⁶ and the solar energy route,⁷ *etc.* Among these techniques, the arc-discharge and laser ablation methods often yield high-quality products, however, it is difficult to scale up the production. As a result, the CVD method has become more popular and is considered at the moment to be the best approach for low-cost and large-scale synthesis of high-quality nanotube materials.^{8–10}

Chemical vapor decomposition of hydrocarbonates over metal catalysts is a useful method which can be employed to obtain various forms of carbon materials,¹¹ such as carbon fibers, filaments and carbon tubes, *etc.* More recently, it has been found that the CVD method could be also effective for the synthesis of SWNTs by suitably preparing the catalyst materials and controlling the reaction conditions. For instance, Peigney *et al.* obtained a mixture of single- and multi-walled nanotubes by methane CVD on Fe alumina nanocomposites.¹² Dai synthesized SWNT by the disproportionation of CO on Mo nanoparticles and the decomposition of methane on silica/alumina supported Fe, Co or Ni oxide catalysts.^{9,13} Liu and co-workers were successful in greatly improving the yield of SWNTs by using an alumina aerogel supported Fe/Mo catalyst.¹⁰ SWNTs can also be successfully prepared from other kinds of carbon sources and supported catalyst materials.^{14–17} Although the understanding of the relationship between the catalyst and the nanotube growth process is still superficial, the choice of support material has been found to be

critical for scalable CVD synthesis of high quality SWNTs. In our research, we found that MgO, especially the porous MgO obtained by thermal decomposition of Mg salts, is an excellent support material for the CVD synthesis of high-purity SWNTs; the addition of assistant-catalyst Mo salts can increase the production yield to about 120%. In the present study, the effects of different reaction conditions on the structure and purity of SWNTs were investigated in detail, including catalyst type, reaction temperature, flow rate of the reaction gas and purification procedures.

2 Experimental

The MgO supported materials used in our experiments were obtained by three routes: one was the chemical reagent used as purchased, the other two were obtained by thermal decomposition of Mg nitrates and alkaline magnesium carbonates at 400 °C, respectively. Of the other types of support used in our work, SiO₂ (BET surface area: 400 m² g⁻¹) was synthesized by calcining the product from the sol-gel process of TEOS (tetraethoxysilane) at 400 °C,¹⁸ ZrO₂ (BET: 157 m² g⁻¹) was synthesized by adding 4 M ZrOCl to 25% ammonia solution and then calcining the precipitate at 400 °C,¹⁹ and CaO (BET: 5 m² g⁻¹) was obtained by thermal decomposition of Ca carbonate at 400 °C. All the supported catalysts used in our experiments were prepared by sonicating the support material in an aqueous nitrate solution of Fe, Co or Ni at the desired concentration (weight ratio: 10–50%) for several minutes. The resulting mixture was then dried at 115 °C for at least 5 hours, and then ground into a fine powder for use.

SWNTs were prepared in a simple CVD setup made of a tube furnace and gas flow control units. In a typical growth experiment, about 1 g catalyst was put into an alumina boat inside a quartz tube and was heated to reaction temperature (normally 850 °C) under an Ar atmosphere at a flow rate of

250 ml min⁻¹; the reaction began when methane gas was introduced into the Ar gas. After the SWNTs had been allowed to grow for the desired time (typically 30 min), the methane gas was turned off and the furnace was cooled to room temperature under an Ar atmosphere. The catalyst and support material were finally removed by dissolution in 4 M hydrochloric acid.

TEM, SEM, micro-Raman and TG were employed to characterize all of the CVD grown samples. TEM was performed on a Hitachi H810 at 20 kV; sample preparation involved sonicating the synthesized materials in 2% surfactant solution for at least half an hour, and then placing a few drops of the resulting suspension onto holey carbon grids. SEM was conducted at 25 kV using a Hitachi H-800 field-emission instrument. To prepare samples for SEM, the treated materials were sonicated in dichloromethane for 10 min, and a few drops of the suspension were placed onto the silicon substrate and allowed to evaporate. Micro-Raman experiments were carried out with a Renishaw system 1000 in the ambient atmosphere and at room temperature; Raman spectra were recorded using a 50 mW He-Ne laser, operating at 632.8 nm, and a CCD detector. The final spectra presented were obtained by averaging at least 15 spectra recorded at different points over the entire sample surface.

3 Results and discussion

3.1 The effect of the support material

It is well known that in a catalytic reaction, the properties of support materials including their chemical composition, surface area, pore size and porosity, may affect the properties and yield of the product. For CVD synthesis of carbon nanotubes, it has been found that the type of support material can result in different interactions between the support and catalysts, and therefore affect the growth mechanism of the carbon tubes.²⁰ SiO₂, Al₂O₃, MgO, CaO and ZrO₂ are commonly used support materials in catalytic reactions, and these have therefore been chosen to prepare various supported Fe oxide catalysts for SWNT growth. As SWNTs are Raman active and can exhibit the characteristic radial breathing mode (RBM) at low frequencies unlike MWNTs, micro-Raman spectroscopy is an efficient and simple method to characterize as-prepared samples, and it may also provide a great deal of information on the nature of the synthesized SWNT samples.^{21,22} For a typical SWNT sample, three modes are often seen in its Raman spectrum. The RBM centered around 200 cm⁻¹ can be used directly to estimate the diameters of the SWNTs. The G-line mode located around 1580 cm⁻¹ is assigned to several C-C bond motions due to the introduction of curvature into the graphite sheet, and it depends weakly upon the diameter and helicity of the SWNTs. The D-line centred around 1350 cm⁻¹ is usually ascribed to carbon impurities present in the bulk samples. Although SWNTs have a weak feature in this region, the Raman intensity ratios between the G-line and D-line peaks is often used to estimate the purity of the tube samples.²³

Under the same experimental conditions, the five kinds of supported catalyst, including SiO₂, Al₂O₃, MgO, CaO and ZrO₂, all became black after methane CVD at 850 °C. However, the results of Raman characterization were quite different. On SiO₂, ZrO₂ and CaO supported catalysts, we did not observe the RBM at low frequency, indicating that no SWNTs had formed. Although for alumina, not all the sources of the materials may give rise to the formation of SWNTs, in the case of α -Al₂O₃ or Al₂O₃ prepared by precipitation of diasporite with CO₂, no RBMs were observed in their Raman spectra, which suggested that the growth of SWNTs depended upon the crystal structures of the alumina used. However, SWNTs could be grown on various MgO obtained by different routes (as seen in Table 1).

In our experiment, the MgO samples were obtained by three

Table 1 Textural properties of the investigated support materials

Material	BET areas/m ² g ⁻¹	Average pore size/nm	RBM peak	I _G /I _D
SiO ₂	446	7.2	No	
CaO	4.8	38	No	
ZrO ₂	105	22	No	
Al ₂ O ₃	155	15	Yes	2.3
MgO	10	25	Yes	1.9
MgO-Mg(NO ₃) ₂	32	14.2	Yes	12.5
MgO-Mg(CO ₃) ₂ in air	50	16.2	Yes	12.8
MgO-Mg(CO ₃) ₂ in Ar	66	12.8	Yes	14.0

routes: one was directly from the chemical reagent (called route I), the other two were from the thermal decomposition of Mg nitrate and alkaline Mg carbonate at 400 °C, called routes II and III, respectively. The BET areas of each sample were 10, 32 and 50 m² g⁻¹, and the average pore diameters were 25, 14.2 and 16.3 nm respectively. As shown in Fig. 1, comparison between the resulting Raman spectra of the three kinds of carbon products formed revealed that MgO from route I resulted in a D-line with the highest intensity, suggesting that there were more carbon impurities in the bulk sample. In contrast, MgO obtained by thermal decomposition using routes II and III showed higher BET areas and porosity and resulted in the growth of tube samples with higher purity. The results of Raman characterization were in good agreement with the results of SEM imaging. However, the diameters of as-prepared carbon tubes were found to be independent of the pore size and BET area of the MgO materials. The yields of production of carbon materials on these supports were all around 10%, which also indicated that the BET areas of the materials investigated in our work had little influence on the productivity for SWNT growth.

Another interesting phenomenon found in our experiments was that the particle sizes of the MgO material obtained by decomposition of Mg salts in flowing Ar were more uniform than those obtained in air. The results of the BET measurements shown in Table 1 indicate that MgO obtained in flowing Ar had a larger BET area and smaller pore diameter than that prepared in air. In addition, the Raman spectra at each site on the sample were more consistent. Although there was no evident difference in the RBM bands, the D- and G-lines for the case in air were shifted to higher frequency (see Fig. 1). The ratio of I_G/I_D in flowing Ar was also higher than that in air.

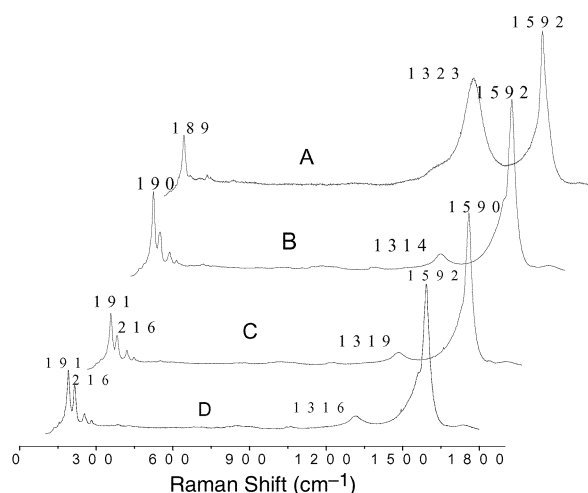


Fig. 1 Raman spectra of as-prepared SWNTs on MgO support materials obtained by different routes, A: from the chemical reagent; B: from the decomposition of Mg nitrite; C: from thermal decomposition of alkaline Mg carbonate in air; D: from thermal decomposition of alkaline Mg carbonate in flowing Ar.

This suggested that the uniform particle size distribution and the support with small pore sizes favored the formation of SWNTs with higher purity. As MgO obtained by the thermal decomposition of alkaline Mg carbonate in flowing Ar showed the highest ratio of I_G/I_D (indicating that it was quite favorable for the growth of high-purity SWNTs), it was used as the support material for the preparation of various catalysts in the following experiments.

On the basis of the above phenomenon, it could be concluded that among the supports used in the study, MgO, especially porous MgO obtained by the thermal decomposition of Mg salts, seemed to be more efficient in the production of SWNTs. The quality of as-grown SWNTs could be improved by tuning the nature of the MgO. In addition, using MgO as the support material may present other advantages, as it can be easily removed in mild acid, which means that less damage would be caused to the native properties of the carbon tubes. So in this regard, SWNT growth could be easily scaled up for industrial use.

3.2 The effect of reaction conditions

Fig. 2 shows the Raman spectra of SWNTs grown on MgO supported Fe catalyst ($W_{Fe(NO_3)_3}:W_{MgO} = 10\%$) at different temperatures. Below 600 °C, no SWNTs formed; when the furnace temperature was elevated to higher than 700 °C, SWNTs grew well. But when the temperature was higher than 1000 °C, the D-line became stronger, and the outer wall of the ceramic boat was found to be covered with black deposits, which indicated that more carbon impurities were present in the bulk samples. The optimal temperature for SWNT growth was thus in the range of 700–950 °C. Over this temperature range, we observed that there were four peaks in the RBM region. At lower temperatures, the strongest peak was located at 189 cm^{-1} , which could be roughly estimated as 1.18 nm according to Bandow's equation.²⁴ The peak at 215 cm^{-1} increased obviously with an increase in temperature, suggesting that the growth of smaller diameter SWNTs was favored at higher temperatures. Additionally, the D-line was found to be red-shifted with an increase in furnace temperature, while the G-line was almost unchanged. The ratio I_G/I_D increased with furnace temperature, indicating that more disordered carbon material was present in the bulk samples at higher temperatures.

Fig. 3 shows the effect of flow rates of the carrier and reaction gas on SWNT growth. It was observed that increasing the proportions of methane over Ar yielded more disordered carbon. Conversely, highly pure SWNT products could be

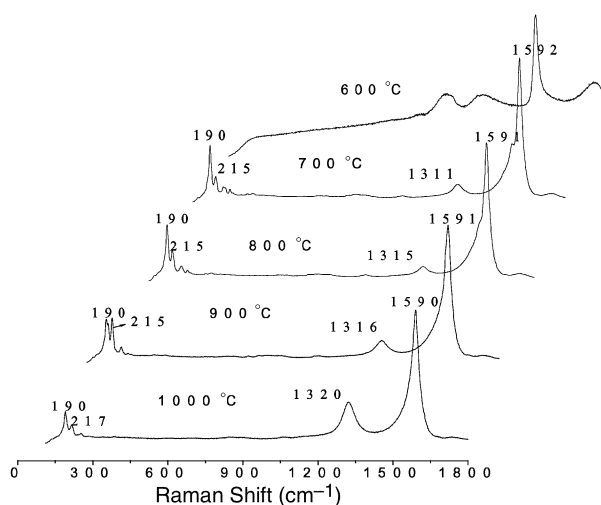


Fig. 2 Raman spectra of bulk SWNTs samples synthesized at different furnace temperatures.

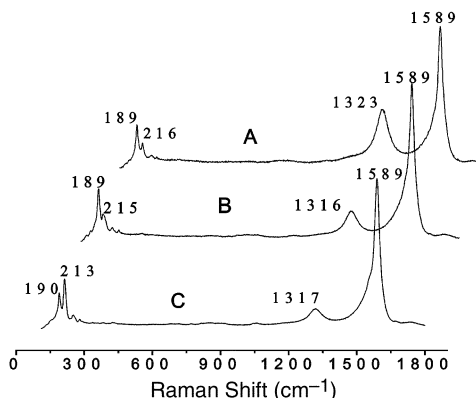


Fig. 3 Raman spectra of SWNT samples synthesized at different flow rates of the gases A: Ar:CH₄ = 1:5; B: Ar:CH₄ = 5:1; C: Ar:CH₄ = 10:1.

obtained with higher ratios of Ar to methane. This result was reasonable, since when larger quantities of methane molecules flow over the catalyst, they would not be able to react sufficiently with the dispersed metal particles, thus yielding more carbon impurities in the bulk sample.

3.3 The effects of catalyst composition

Some metal particles may catalyze either the reduction or oxidation reaction of methane. It has been generally considered that the specific catalytic activity of these metal particles depends not only on their native properties, but also on the interaction between the metal particles and the support material.²⁵ MgO possesses a great number of alkaline reaction sites, and some metal oxides have been verified to be able to disperse well over it even at higher temperatures.²⁶ This may be an important reason why MgO is so successful for SWNT growth. A variety of MgO supported metal catalysts were prepared using the impregnation method with the weight ratios of metal salts to MgO all kept at 10%. As shown in Fig. 4, unlike the Cu, Mo and Mn salts, the Fe, Co and Ni salts exhibited high catalytic activity for SWNT growth. From the Raman spectra, we observed that the Ni based catalyst favored the formation of SWNTs with a narrow range of diameter distribution, the least amount of disordered carbon was produced with the Co based catalyst, and the appearance of another peak at 1560 cm^{-1} was attributed to the special electric properties of the resulting SWNTs.²⁷ From the viewpoint of purification, however, the Fe based catalyst was more favorable for SWNT production, as the oxides of Co and Ni

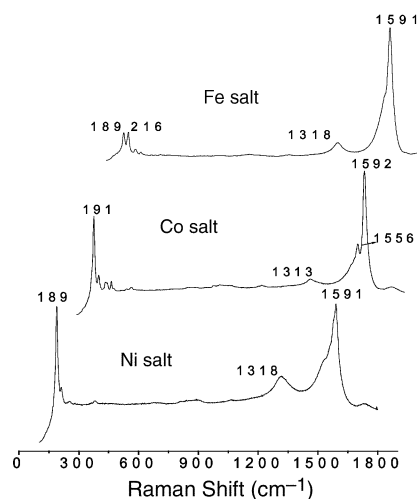


Fig. 4 Raman spectra of as-grown SWNTs on different kinds of MgO supported catalysts.

were slightly soluble in mild HCl and could not be easily removed.

3.4 Improvement of the yield and purity of prepared SWNTs

On the basis of the above experimental results, we can conclude that MgO supported Fe oxide catalysts are favorable for SWNT growth with high purities. Besides the purity, the yield of SWNTs was also an important parameter for evaluating the feasibility of a particular synthetic method. Mo salt was often added to prepare the catalyst, as it has been found to be of some help for the prevention of aggregation of the metal oxide particles on the support materials.²⁸ Thus, in our experiment, we investigated the influence of the amount of Fe salt loaded on MgO and the further addition of Mo salt to the catalyst on the yield of SWNT product. In this experiment, we used MgO obtained from route III as the support material and Fe nitrate solution as the impregnation solution to prepare MgO supported Fe based catalysts for SWNT growth. SWNTs were synthesized on MgO supports loaded with different amount of Fe salts (weight ratio from 5 to 50%). A small amount of hexaammonium heptamolybdate tetrahydrate (weight ratio with respect to MgO) was further added according to requirements. During the growth of nanotubes, the furnace temperature was kept at 850 °C, the flow rates of Ar and methane were kept at 250 and 60 ml min⁻¹, respectively. The carbon yields reported in the present study were calculated by the weight loss of as-prepared black products divided by the weight left at 850 °C.

Fig. 5 reveals the dependence of the yield of SWNTs on the loading quantities of Fe nitrate before and after the addition of Mo salt. It was found that the yield of SWNTs on the catalyst was less than 25% even if the loading of Fe salts was as high as 40%. But the yield (120%) increased greatly when a small amount of Mo salt was added to the catalyst. It was almost five times higher than the yield without Mo salt and also much higher than that reported in the previous work by Colomer.¹⁹ However, we also found that a higher yield of carbon material may be at the expense of the purity of the SWNT samples to some degree. As a result, the optimal loading amount of Fe salts on the MgO support should be confirmed in order to maximize both the production yield and the purity of products. We ultimately found that a loading capacity of 10% on the MgO support was satisfactory for SWNT growth with high purity.

Under the reaction conditions recommended above, the carbon materials were synthesized in about 1 g quantities each time. After removal of the MgO support and Fe oxide by refluxing the bulk sample in 4 M HCl for several hours, the purified sample was then characterized by SEM, TEM, and TG techniques. As shown in Fig. 6A, the abundant rope-like nanotube networks were observed by SEM; the support material and other contaminants could hardly be found in

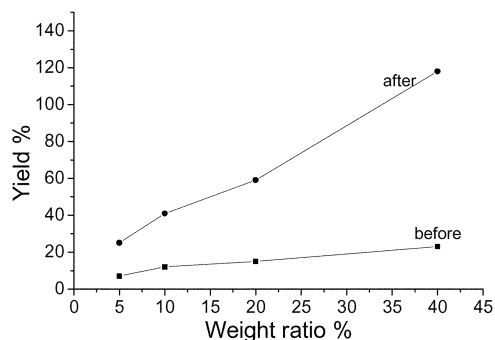


Fig. 5 The yield of SWNTs prepared on MgO supported Fe oxide catalysts before and after the addition of Mo salts.

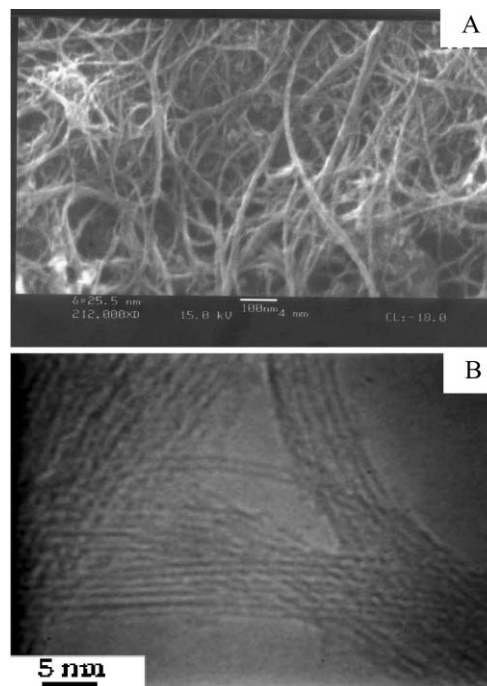


Fig. 6 SEM (A) and TEM (B) images of purified SWNTs in 4 M HCl.

the sample. High magnification TEM images revealed that the synthesized material consisted of high quality individual and bundled single-walled nanotubes (Fig. 6B). A characteristic Raman spectrum of the purified sample could also be obtained, and little difference was found in the Raman spectra of SWNT samples before and after the treatment step. In TG curves, the weight loss between 200 and 700 °C was about 90%, and the appearance of only one peak at about 560 °C also confirmed that there was little disordered carbon material in the SWNTs samples, as the characteristic combustion temperature of disordered carbon usually emerges at around 400 °C. The combustion temperature of the SWNTs in our work was consistent with the reported value²⁹ for SWNTs that were obtained by the arc-discharge method. This implies that the quality of the as-grown SWNTs in our work was high.

4 Conclusions

As nanotubes can be utilized individually or as an assembly for versatile uses, low-cost, scalable and controllable synthesis of high quality carbon nanotube materials is of great significance. Compared to other kinds of methods, CVD methods are likely to be the best approach to achieve this aim. Although much effort has been made in this area and many successes achieved, the mechanism of nanotube growth, especially SWNT growth is still beyond our grasp. As a result, extensive and detailed studies on CVD synthesis of SWNTs may be of great help in accumulating experience of carbon tube growth. Generally, support materials and catalysts are the main factors for successful CVD growth of SWNTs. In our work, we found that porous MgO was an eminent support candidate for high-quality SWNT growth. By properly controlling the reaction parameters, such as furnace temperature, catalyst preparation and flow rate of the gas, *etc.*, we could obtain SWNT products with fewer impurities, higher yields and controllable diameters. As MgO can be easily removed with mild acid, the purification of SWNTs with mild acids may cause little damage to the structures of the as-prepared products. It would thus be helpful for us to obtain more information on their pristine properties.

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References

- 1 S. Iijima, *Nature*, 1991, **354**, 56–59.
- 2 S. Iijima, *Nature*, 1993, **363**, 603.
- 3 T. W. Ebbesen and P. M. Ajayan, *Nature*, 1992, **358**, 220.
- 4 A. Thess, R. Lee and R. E. Smalley, *Science*, 1996, **273**, 483.
- 5 J. Kong, A. M. Cassell and H. Dai, *Chem. Phys. Lett.*, 1998, **292**, 567.
- 6 R. L. Vander Wal and T. M. Tichich, *Chem. Phys. Lett.*, 2000, **324**, 217.
- 7 D. Laplaze, P. Bernuer and W. R. Master, *Carbon*, 1998, **36**, 685.
- 8 H. Dai, *Top. Appl. Phys.*, 2001, **80**, 29.
- 9 A. M. Cassell, J. A. Raymakers, J. Kong and H. Dai, *J. Phys. Chem.*, 1999, **103**, 6484.
- 10 M. Su, B. Zheng and J. Liu, *Chem. Phys. Lett.*, 2000, **322**, 321.
- 11 G. G. Tibbetts, *Carbon*, 1989, **27**, 745.
- 12 A. Peigney, Ch. Laurent, F. Dobingon and A. Rousset, *J. Mater. Res.*, 1997, **12**, 613.
- 13 H. Dai, *Chem. Phys. Lett.*, 1996, **260**, 471.
- 14 H. M. Cheng, F. Li, G. Sun and H. Pan, *Appl. Phys. Lett.*, 1998, **72**, 3282.
- 15 E. Flahaut, A. Govindaraj and A. Peigney, *Chem. Phys. Lett.*, 1999, **300**, 236.
- 16 X. P. Gao, X. Qin and F. Wu, *Chem. Phys. Lett.*, 2000, **327**, 271.
- 17 J. F. Colomer, C. Stephan and S. Lefrant, *Chem. Phys. Lett.*, 2000, **317**, 83–89.
- 18 K. Kanichi, D. Tomori and W. Masanori, *J. Non-Cryst. Solids*, 1998, **240**(1–3), 202.
- 19 S. Ardizzone, G. Bassi and G. Liborio, *Colloids Surf.*, 1990, **51**(23), 207.
- 20 N. Franklin and H. Dai, *Adv. Mater.*, 2000, **12**, 890.
- 21 A. M. Rao, S. Bandow and E. Richter, *Thin Solid Films*, 1998, **331**, 141.
- 22 A. Claye, S. Rahman and J. E. Fischer, *Chem. Phys. Lett.*, 2001, **333**, 16.
- 23 H. Kataura, Y. Kumazawa and Y. Maniwa, *Carbon*, 2000, **38**, 1691.
- 24 S. Bandow, S. Asaka, Y. Saito and A. M. Rao, *Phys. Rev. Lett.*, 1998, **80**(17), 3779.
- 25 J. F. Colomer, G. Bister and I. Willems, *Chem. Commun.*, 1999, 1343.
- 26 S. B. Wang, H. Y. Zhu and G. Q. Lu, *J. Catal.*, 1998, **204**, 128–134.
- 27 M. A. Pimenta, A. Marucci, D. M. Brown and R. E. Smalley, *J. Mater. Res.*, 1998, **13**, 2396.
- 28 M. C. Abello, M. F. Gomez and O. Ferretti, *Appl. Catal., A*, 2001, **207**(1–2), 421.
- 29 Z. J. Shi, Y. F. Lian and Z. N. Gu, *Solid State Commun.*, 1999, **112**, 35.