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Wet catalyst assisted growth of carbon nanofibers on complex three-dimensional substrates

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Abstract

Carbon nanofibers are grown from different organo-metallic catalysts by thermal and plasma-enhanced chemical vapour deposition on complex three-dimensional foam and cloth substrates. With a suitable deposition arrangement, we can achieve uniform coverage by using Ni formate and Co colloid catalysts instead of evaporated or sputtered thin metal films. Chemical vapour deposition (CVD) allows the direct growth of carbon nanofibers onto these substrates with good surface adhesion. The use of plasma-enhanced CVD enables fiber alignment and a low deposition temperature, down to 250 °C.
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1. Introduction

The unique mechanical, thermal and electrical properties combined with chemical inertness and a high surface area make carbon nanotubes (CNTs) and nanofibers (CNFs) a very attractive material for an increasing number of applications such as reinforcement in composites [1–3], supercapacitors [4–7], nanofilters and -sensors [8], fuel cells [9] and batteries. For electrochemical applications stacked, herringbone or generally more defective CNFs offer a more active surface and possible intercalation between the graphene layers [10].

For many of the applications, it is desirable to grow the CNTs/CNFs directly onto a specific support with good adhesion and no bundling of the nanofibers. Chemical vapour deposition (CVD) allows the direct growth on a surface if this is pre-patterned with a metal catalyst. A particular challenge is the growth on complex substrates such as foams, meshes or cloths often used in electrochemistry. The directionality of the conventional metal catalyst deposition techniques, such as evaporation or sputtering, leads to a shadowing of substrate areas facing away from the source, thereby resulting in a very inhomogeneous or incomplete coverage.

Here, we present a CVD growth study exploring the use different wet catalyst systems on foam and cloth substrates. We show that Ni formate and Co colloid catalysts can give a homogeneous coverage of non-planar, complex surfaces over large areas and at low cost. An additional plasma enhancement allows the vertical alignment of the as-grown CNFs and a low deposition temperature down to 250 °C. This low temperature widens the range of possible substrates to include plastics [11–13] and textiles [1].

2. Experimental

Fig. 1 shows the substrates used in the present work: Ni foam and carbon cloth. The Ni foam (Fig. 1(a)) has a density
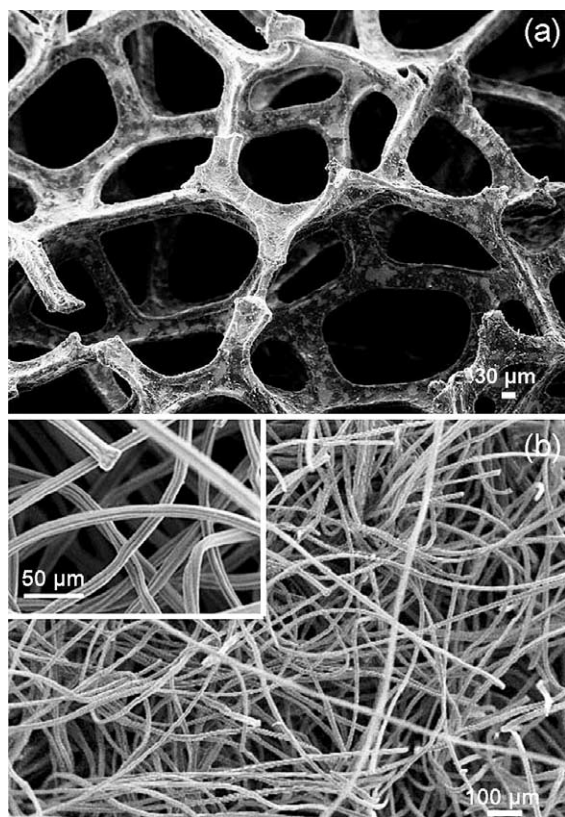

Fig. 1. SEM images of (a) Ni foam and (b) carbon cloth substrates.

of 400 g/m^2 and regular pores ~500 μm in diameter ensuring good accessibility of an electrolyte into the matrix. The carbon cloth (Fig. 1(b)), from Morgan Specialty Graphite, Fostoria, Ohio (USA), consists of carbon fibers ~10 μm in diameter, entangled in a 3D matrix. The thickness of the cloth is ~2.5 mm.

As wet catalyst, in the case of Ni foam, we used a Ni formate solution. For electrochemical applications, no metals other than the foam material are desired. The Ni formate solution (2.2×10^{-2} M) is made by dissolving Ni formate in methanol and adding a surfactant to improve substrate wetting. Ni formate undergoes dehydradation and thermal decomposition as temperatures goes up during the thermal ramp in the CNF deposition process [14], leaving only Ni particles by the following reaction, occurring at ~260 °C [15]:

$$Ni(HCOO)_2 \rightarrow Ni + H_2 + 2CO_2$$

Ni clusters tend to sinter under conditions given by Ni concentration, surface interactions and deposition parameters.

As catalyst for the carbon cloth, we used a Co colloidal solution, prepared by the inverse micelle method [16]. A master solution of AOT (bis(2-ethylhexyl) sulfo succinate Na salt) stabilized Co colloid undergoes several chemical processing cycles, involving purification, flocculation and centrifugation. To minimize sintering or Ostwald ripening effects [17], a surfactant is used to passivate the

colloid nanoparticles. The detailed preparation procedure is reported elsewhere [18]. Before applying the Co colloid on the cloth, we performed another centrifugation step to narrow down the Co particle size distribution and cut off the fraction of larger particles. The resulting colloid has a diameter distribution around 2–4 nm, as confirmed by high-resolution transmission electron microscopy (HRTEM), Fig. 2. We then wetted the cloth samples (~5×5 mm^2 size) by repeated soaking into the solution and then let them dry in an inert atmosphere. Repeated cycles can improve the cloth fiber coverage, and thus the CNF growth yield.

The CNFs growth on Ni foam was done by thermal CVD. The CNFs growth on carbon cloth was done by dc-PECVD. Both CVD and PECVD growth can be performed in the same deposition chamber, as previously described [11]. The substrates are placed onto a graphite stage heater. Gas is provided by an inlet placed about 2 cm above it. The substrates are then annealed for 15 min in 200 sccm NH$_3$ (1.2 mbar) until the final deposition temperature is reached. For plasma-enhanced growth, the dc discharge is started by applying 600 V between the sample heater stage (cathode) and the gas inlet working as anode. C$_2$H$_2$ is used as carbon feed gas, with a gas mixture ratio of 200:50 sccm NH$_3$/C$_2$H$_2$ (1.5 mbar) during deposition. The discharge is kept constant for 30 min. Teo et al. [19] argued that high power plasmas can result in very high temperatures at the substrate holder in a dc-PECVD system. They reported a substrate temperature of 700 °C for 200 W plasma power, even in the absence of additional heating. In this condition, they observe an intense glow in the cathode region [19]. In contrast, it is important to notice that in our case the average plasma currents are in the 30–40 mA range and deliver a total power of only ~20 W. This guarantees the minimization
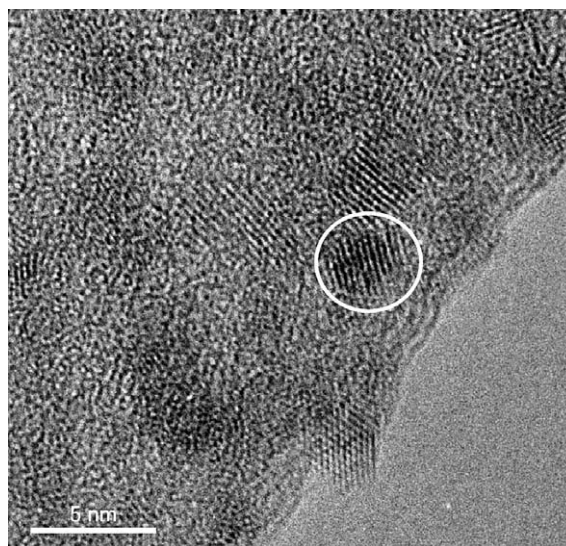

Fig. 2. HRTEM image of Co nanoparticles in the as-prepared colloidal solution. The circle encloses a typical Co nanoparticle. The diameters are in the 2–4 nm range, including the surfactant shell.

of plasma heating effects. Indeed, we do not observe any glowing in the cathode region, nor any significant heating effects. The local temperature was measured embedding a thermocouple into the sample matrix and ensuring a good thermal contact. The gas ratio we use is effective in avoiding unwanted amorphous carbon deposition, due to the etching effect of NH_3 [11,20].

The size and crystalline structure of the CNFs were analyzed by scanning electron microscopy (SEM, Jeol 6340 FEGSEM), HRTEM (Jeol 4000EX, 400 kV) and Raman spectroscopy (Renishaw 1000 spectrometer, 514.5 nm laser excitation). For HRTEM analysis, individual cloth fibers were removed from the cloth matrix and dispersed onto Cu grids.

3. Results and discussion

Large-scale accurate 2D patterning of colloidal catalysts by conventional lithography is more challenging than sputtering or evaporation of thin films. However, we have recently shown that sub-micrometer stripes and dots of colloidal catalyst can be successfully patterned by nano-contact printing [21] onto flat Si substrates and we have then grown patterned CNFs at low temperature [22]. Here, we take a further step considering the case of uniform 3D application of the colloids.

It was previously reported that CNF growth can be achieved across all the bulk of 3D substrates. For example, Smiljanic et al. [23] used a CVD configuration in which the feeding gas is blown from one side of the quartz reactor and it flows along the furnace axis across a carbon paper substrate with its surface perpendicular to the flow axis. Here, we demonstrate that the 3D growth can also be achieved in PECVD conditions at low temperature in more complex substrates such as carbon cloth. Literature reports a recent example of CNF growth on polyacrylonitrile (PAN) electrospun fibers, using Fe(acetylacetonate)₃ as catalyst [24]. The sub-micrometer diameter PAN fibers were synthesized and catalyst-treated, to be ready for the thermal CVD growth of CNFs, in a multiple-step processing route. However, we decided to employ an available commercial product such as the mentioned carbon cloth as substrate.

We first consider what happens if one applies the catalyst on carbon cloth by conventional sputtering. Fig. 3(a) and (b) show that the CNF yield is significant for both dc-PECVD and thermal growth, at a temperature of 400 °C. However, in both cases, as demonstrated by Fig. 3(b), there are areas of the carbon fibers not covered by CNFs because no catalyst is present. This shadowing effect is the main drawback of the standard 2D catalyst coating techniques. Sputtering (and, more generally, any physical vapour deposition technique) is thus unsuitable to provide uniform catalyst coverage on complex 3D materials.
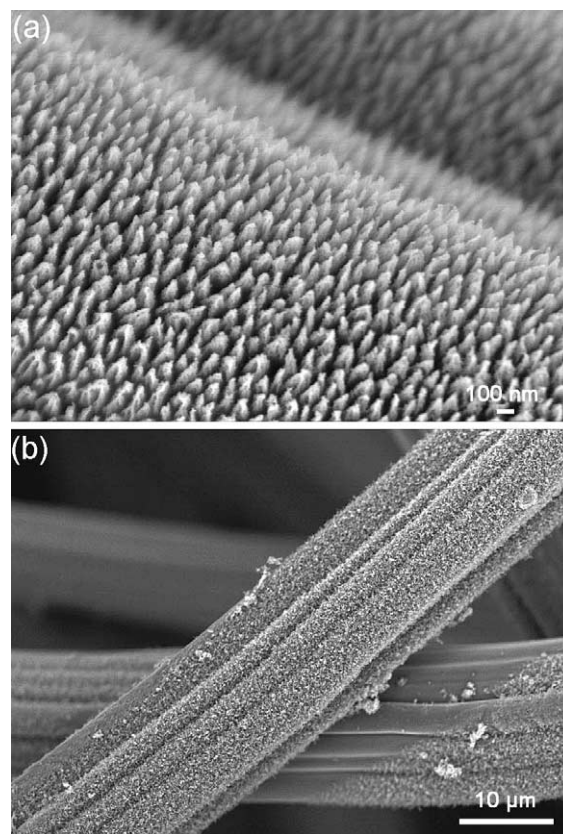

Fig. 3. SEM images of CNFs grown by using sputtered Ni catalyst on carbon cloth fibers by (a) dc-PECVD and (b) thermal CVD at 400 °C.

As wet catalysts, we first used a Ni formate solution to impregnate the Ni foam. Fig. 4(a) and (b) show CNFs grown by thermal CVD on the Ni foam at 500 °C. Although untreated Ni foam itself catalyzes CNF growth, a more dense and uniform CNF coverage is found using Ni formate as catalyst and the crystallinity of the grown structures is much higher. We also found a dependence of the CNF yield on the soaking stages, but not of the CNF diameter distribution. No pre-treatment stage was performed on the Ni foam to improve wetting by the Ni formate. Results of hydrogen exchange tests performed on the CNF-covered Ni foam demonstrate the good adhesion of the grown structures onto the 3D matrix and that the technique is promising for electrochemical applications.

In another set of experiments, we impregnated carbon cloth with Co colloid. The substrate was then transferred into the deposition chamber. Using the heater stage set-up already mentioned, the CNF coverage was localized to the top layers of the carbon cloth substrate. However, coverage could be improved modifying the substrate exposure to the gas flow. We drilled a hole through the heater stage and placed the substrate partly over it, so that the gas is blown directly through the cloth bulk. We found that cloth fibers on the top and bottom layers of the bulk were covered by CNFs, enhancing the effectiveness of this approach.
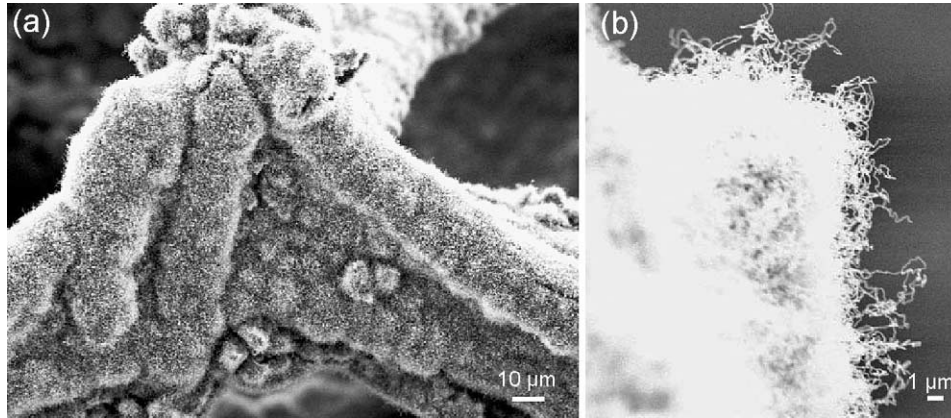
Fig. 4. SEM image of CNFs grown on Ni foam by thermal CVD at 500 °C, using Ni formate as catalyst.

Fig. 5(a) shows CNFs grown on cloth at a temperature of 400 °C. The CNF coverage is uniform, due to the uniform wetting of the cloth fibers by the colloid. CNFs have a narrow diameter distribution, with diameters below 40 nm. The growth rate is ~1 nm/s. The CNF alignment induced by the plasma electric field can also be seen. As for Ni foam, we stress that no pre-treatment of the cloth fibers was performed to improve the CNF adhesion. Fig. 5(b) and (c) show details of the bottom and top areas of the covered cloth fiber in Fig. 5(a). It is often reported (e.g. [20,25]) that PECVD-grown CNFs tend to align in the direction of the electric field induced by the plasma. If the substrate is

conductive, this results in growth perpendicular to it. This plasma-induced alignment is completely different from the one observed in CVD growth [26–28], where a similar alignment is due to a "crowding effect" induced by the Van der Waals attraction between the individual fibers. We generally expect CNFs to grow radially on the cloth fibers, due to plasma alignment, such as in Fig. 5(b). However, Fig. 5(a) shows that this is not always the case. Plasma screening could be a reason for this.
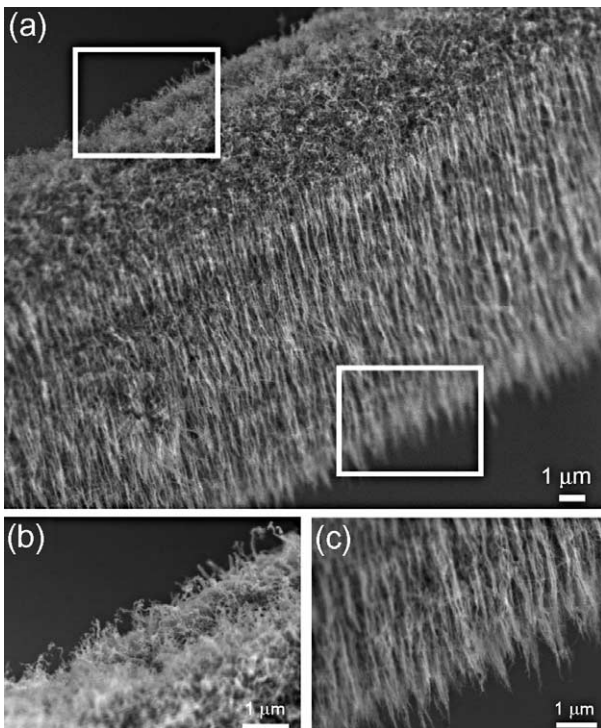

Fig. 5. (a) SEM image of CNFs grown on carbon cloth at a temperature of 400 °C, using Co colloid as catalyst. (b) and (c) are higher magnification images of the regions delimited by white squares in (a).
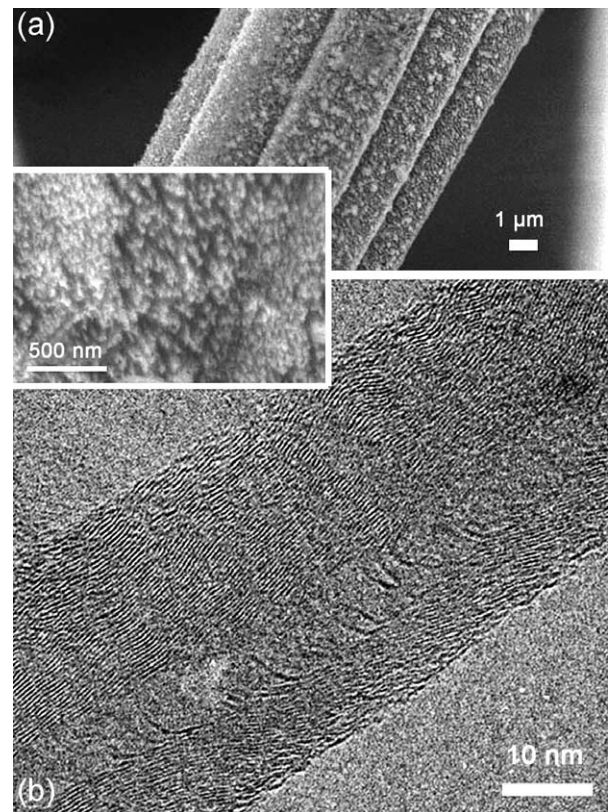

Fig. 6. (a) SEM image of CNFs grown on carbon cloth at a temperature of 250 °C, using Co colloid as catalyst. (b) is a higher magnification image of (a) showing that the coverage is still significant. (c) HRTEM image of a single CNF grown at 250 °C. A typical bamboo-like structure is evident.

Fig. 6(a) shows that the coverage of the cloth fibers is still significant at temperatures as low as 250 °C. HRTEM analysis shows a bamboo-like crystalline structure of the grown CNFs (Fig. 6(b)). Co particles are found on CNF tips, suggesting a tip growth mechanism. CNFs have a diameter of about the same size of the Co particle at their tips, indicating that some sintering of the Co catalyst happens prior to the CNF growth process, since the CNF diameter is bigger than the original Co catalyst size.

Raman measurements at 514.5 nm on our samples show the separate contribution of carbon cloth and nanofibers (Fig. 7). Fig. 7(A) shows the Raman spectrum of the uncoated cloth substrate. Fig. 7(B) shows the Raman spectrum of CNFs grown on similar conditions on a Si substrate. The spectrum in Fig. 7(C) is measured on a CNF-coated carbon cloth. The separate contributions of the carbon cloth and the CNFs can be recognized by comparison with Fig. 7(A,B). The D and G peaks of the CNFs are broader than the corresponding peaks in the carbon cloth. This indicates that the CNFs are more structurally disordered than the cloth substrate [20,29].

A careful analysis of the samples shows that, together with CNFs, other high aspect ratio spike-shaped structures are present, Fig. 8. These do not exhibit any plasma-induced alignment and have a wider diameter distribution than the CNFs, with typical diameters often in excess of 100 nm, and a length between 5 and 10 μm. We detected these structures even when using Si as a substrate,

Fig. 8. Spike-shaped structures arise as well as CNFs when Co colloid is used as catalyst.

implying that they are not substrate-dependent. Furthermore, these spikes grow also in thermal conditions, even in absence of a carbon source gas, just by annealing the as-deposited catalyst in NH_3 environment. We thus consider their growth as a side effect of the organic residuals left over from the colloid preparation and handling. Further investigations will be devoted to understand the nature and formation of these structures. It is interesting to note that no CNF growth is observed after annealing the Co colloid-treated carbon cloth in the absence of a carbon containing feed gas. Thus, here, the carbon cloth does not act as a solid carbon source. However, literature reports examples of carbon nanostructures grown by thermal annealing of carbon-based substrates or solid-phase precursors [30,31].

4. Conclusions

We demonstrated the effectiveness of wet catalysts for the growth of aligned, non-bundled carbon nanofibers on substrates with a complex three-dimensional shape. A growth temperature as low as 250 °C was achieved when combining wet catalysis and plasma-enhanced CVD. This paves the way to the creation of high surface area electrodes for applications such as fuel cells, supercapacitors, sensors and to the CNF synthesis onto temperature-sensitive materials such as polymer fibers, textiles and foams.
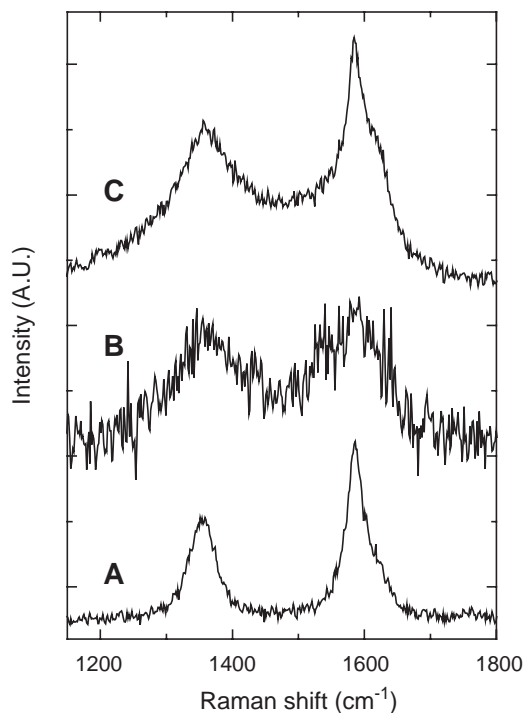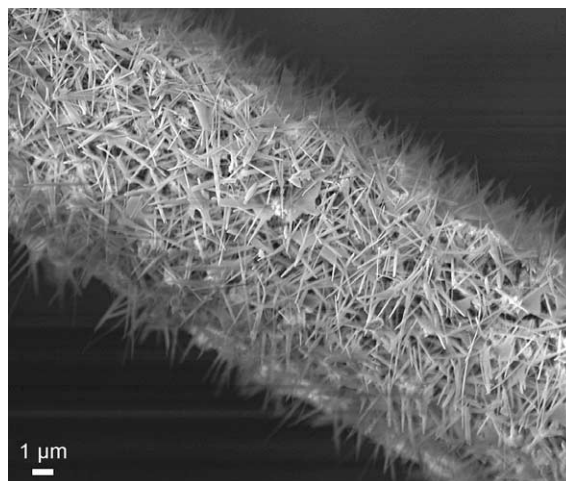
Fig. 7. Raman spectra of (A) untreated cloth substrate; (B) CNFs grown by dc-PECVD and Co colloids catalyst at 400 °C on Si; (C) covered cloth, with CNFs grown in the same conditions as (B).

References

[1] A.B. Dalton, S. Collins, E. Munoz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J.N. Coleman, B.G. Kim, R.H. Baughman, Nature 423 (2003) 703.

[2] Y.L. Li, I.A. Kinloch, A.H. Windle, Science 304 (2004) 276.

[3] M.S.P. Shaffer, A.H. Windle, Adv. Mater. 11 (1999) 937.

[4] C.M. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, Appl. Phys. Lett. 70 (1997) 1480.

[5] E. Frackowiak, F. Beguin, Carbon 39 (2001) 937.

[6] C. Emmenegger, P. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, A. Zuttel, J. Power Sources 124 (2003) 321.

[7] L. Schlapbach, A. Zuttel, Nature 414 (2001) 353.

[8] L.M. Le Leuch, A. Subrenat, P. Le Cloirec, Langmuir 19 (2003) 10869.

[9] C. Wang, M. Waje, X. Wang, J.M. Tang, R.C. Haddon, Y.S. Yan, Nano Lett. 4 (2004) 345.

[10] M. Endo, Y.A. Kim, T. Hayashi, K. Nishimura, T. Matusita, K. Miyashita, M.S. Dresselhaus, Carbon 39 (2001) 1287.

[11] S. Hofmann, C. Ducati, J. Robertson, B. Kleinsorge, Appl. Phys. Lett. 83 (2003) 135.

[12] S. Hofmann, C. Ducati, B. Kleinsorge, J. Robertson, Appl. Phys. Lett. 83 (2003) 4661.

[13] M. Cantoro, S. Hofmann, B. Kleinsorge, G. Csanyi, M.C. Payne, A.C. Ferrari, J. Robertson, Proc. of XVIII international winterschool on electronic properties of novel materials, Kirchberg (Austria), 613 March 2004, AIP, Melville, NY, 2004, p. 81.

[14] J.F. Geng, C. Singh, D.S. Shephard, M.S.P. Shaffer, B.F.G. Johnson, A.H. Windle, Chem. Commun. 22 (2002) 2666.

[15] B. Xia, I.W. Lenggoro, K. Okuyama, J. Am. Ceram. Soc. 84 (2001) 1425.

[16] J.P. Chen, K.M. Lee, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, J. Appl. Phys. 75 (1994) 5876.

[17] R. Boistelle, J.P. Astier, J. Cryst. Growth 90 (1988) 14.

[18] B. Kleinsorge, V.B. Golovko, S. Hofmann, J. Geng, D.A. Jefferson, J. Robertson, B.F.G. Johnson, Chem. Commun. (2004) 1416.

[19] K.B.K. Teo, D.B. Hash, R.G. Lacerdo, N.L. Rupesinghe, M.S. Bell, S.H. Dalal, D. Bose, T.R. Govindan, B.A. Cruden, M. Chhowalla, G.A.J. Amaratunga, J.M. Meyyappan, W.I. Milne, Nano Lett. 4 (2004) 921.

[20] M. Chhowalla, K.B.K. Teo, C. Ducati, N.L. Rupesinghe, G.A.J. Amaratunga, A.C. Ferrari, D. Roy, J. Robertson, W.I. Milne, J. Appl. Phys. 90 (2001) 5308.

[21] H.W. Li, B.V.O. Muir, G. Fichet, W.T.S. Huck, Langmuir 19 (2003) 1963.

[22] V.B. Golovko, H.W. Li, B. Kleinsorge, J. Geng, S. Hofmann, M. Cantoro, D.A. Jefferson, B.F.G. Johnson, W.T.S. Huck, J. Robertson, Appl. Phys. Lett. (submitted for publication).

[23] P. Smiljanic, T. Dellero, A. Serventi, G. Lebrun, B.L. Stansfield, J.P. Dodelet, M. Trudeau, S. Desilets, Chem. Phys. Lett. 342 (2001) 503.

[24] H.Q. Hou, D.H. Reneker, Adv. Mater. 16 (2004) 69.

[25] C. Bower, W. Zhu, S.H. Jin, O. Zhou, Appl. Phys. Lett. 77 (2000) 830.

[26] M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W.K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Nature 388 (1997) 52.

[27] S.S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H.J. Dai, Science 283 (1999) 512.

[28] C. Singh, M.S.P. Shaffer, K.K.K. Koziol, I.A. Kinloch, A.H. Windle, Chem. Phys. Lett. 372 (2003) 860.

[29] A.C. Ferrari, J. Robertson, Phys. Rev., B 61 (2000) 14095.

[30] S. Hofmann, J. Robertson, C. Ducati, R.E. Dunin-Borkowski, Nanotechnology 15 (2004) 601.

[31] V. Derycke, R. Martel, M. Radosvljevic, F.M.R. Ross, P. Avouris, Nano Lett. 2 (2002) 1043.