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Pillar-shaped structures and patterns of three-dimensional carbon nanotube alignments

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Pillar-shaped structures and patterns of three-dimensional multi-walled carbon nanotube arrays have been synthesized by pyrolysis of iron(II) phthalocyanine.

Alignments of carbon nanotubes (CNTs) are particularly important for fabricating functional devices such as field emitters[1–4] and nanoelectronics[5,6] as well as ultrahydrophobic materials.[7] Two-dimensional (2D) aligned nanotubes were obtained previously by using chemical vapor deposition (CVD) over catalyst embedded in mesoporous silica[4,8] or on quartz substrate[9] and over laser-patterned catalysts.[10] Recently, Ren *et al.*[11,12] have reported the synthesis of self-aligned 2D nanotubes on glass substrates by using plasma-enhanced CVD, although this method suffered from complex pre-synthesis manipulations. However, to our knowledge, preparation of three-dimensional (3D) CNT alignments has not been reported. Here, we have developed a simple method for a large-scale synthesis of 3D aligned CNTs normal to the quartz substrate surface without any pre- or post-synthesis manipulations.

A typical experimental procedure was as follows:[13] a clean quartz glass plate ($4 \times 2 \times 0.1$ cm) was placed in a flow reactor consisting of a quartz tube and a furnace fitted with an independent temperature controller. A flow of Ar–H$_2$ (1 : 1, v/v, 20 cm^3 min^{-1}) was then introduced into the quartz tube during heating. After the central region of the furnace reached 950 °C, a quartz boat with 0.5 g of iron(II) phthalocyanine was placed in the region where the temperature was 550 °C. After 5 min heating, CNTs grew in a direction normal to the substrate surface. The CNT samples were examined by scanning electron microscopy (SEM, JEOL JSM-6301F) to characterize their profile, alignment and uniformity. Transmission electron microscopy (TEM, Hitachi H-800, 100 kV) was used to determine the diameters and microstructure of the CNTs. X-Ray photoelectron spectroscopy (XPS) analyses of the samples were performed on a VG ESCALAB 220-IXL spectrometer using an Al-Kα X-ray source (1486.6 eV).

Fig. 1 shows SEM images of 3D regular arrays of nanotubes aligned along the direction perpendecular to the substrate surface. As can be seen in Fig. 1(a), a few pillar-shaped structures of CNTs grow out from the 2D alignments in a well distributed mode. At high magnification, the SEM image [Fig. 1(b)] clearly shows that the pillar-shaped structures dispersed in the middle of the 2D CNT alignments. The CNT posts with a diameter of *ca*. 3.4 μm are 7.8 μm higher than the 2D nanotube alignments, whose height is typically 6 μm from the quartz substrate. The structure is reminiscent of papillose epidermal cells of lotus leaf surfaces that provide very effective water-repellent and anti-adhesive properties against particulate contamination, denoted self-cleaning ability.

A high magnification SEM image (Fig. 2) of an individual nanotube post shows that it is a tubular bundle with a diameter of 2.8 μm and a height of 5.5 μm. A TEM investigation (inset) reveals that the nanotubes composing 3D alignments are bamboo-like multiwalled nanotubes[15] with a diameter of *ca*. 50 nm. The alignment is partially preserved despite the sonication of the raw material in ethanol before deposition of the nanotubes onto the holey carbon film TEM grid. This clearly indicates that the nanotubes of 3D alignments are densely packed and held together by van der Waals interactions.

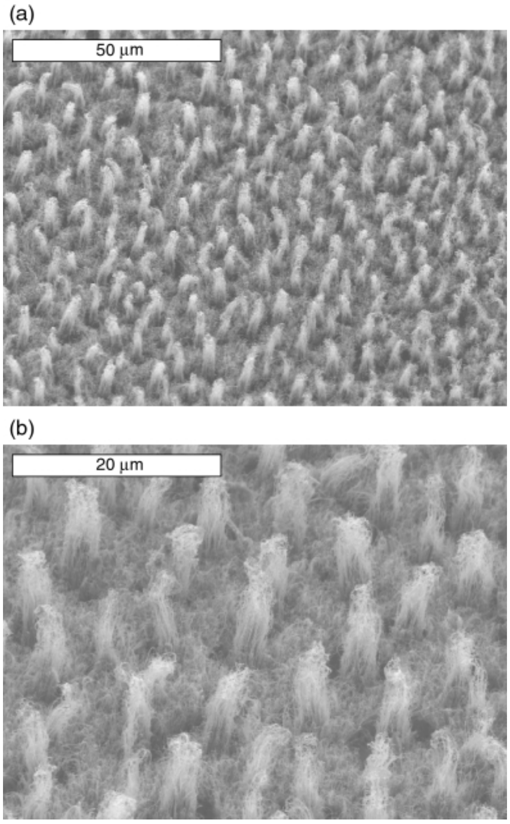

Fig. 1 SEM images of 3D regular arrays of nanotubes aligned along the direction perpendecular to the substrate surface: (a) an oblique 45° of pillar-shaped CNT alignments. (b) a high magnification image of nanotube posts.

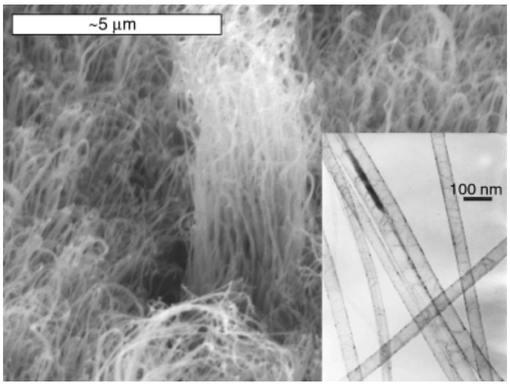

Fig. 2 SEM images of an individual nanotube post from an oblique 45^0 (inset, a TEM image of CNTs).

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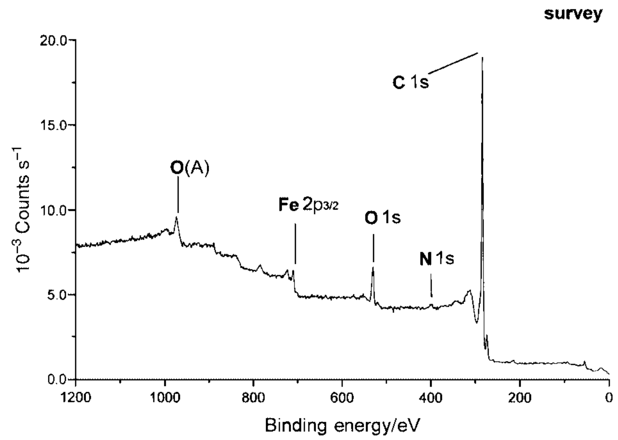

Fig. 3 A wide survey XPS spectrum of the carbon nanotubes.

Fig. 3 shows a wide survey XPS spectrum of the nanotubes. A sharp peak at 284.5 eV corresponds to a π* feature associated with sp^2 hybridized carbon. This observation confirms that the nanotubes mainly contain carbon. Besides carbon (93.30 atom%), nitrogen (0.96 atom%) and iron (0.74 atom%), oxygen (5.00 atom%) is also present in the surface of the nanotubes, which may arise from air absorbed on the nanotubes. A split in the π*-type peak of the N 1s spectrum (not shown) reveals the presence of two peaks at 399.3 and 401.1 eV, corresponding to sp^2 pyridine-like N and sp^3 bridgehead-type N incorporated into the graphitic network, respectively.[16] The 399.3 eV feature is due to pyridinic nitrogen present at the nanotube end, while the peak centered at 401.1 eV corresponds to trivalent nitrogen replacing the carbon in the hexagonal structure.[17] The substitutional N in a graphite sheet strongly favours the formation of pentagons and heptagons, which is responsible for the bamboo-like morphologies.[15]

In addition to the pillar-shaped 3D nanotube alignments, most interesting patterns made of nanotubes arrays, such as ring-like castles [Fig. 4(a)] and a 490 μm long crucian carp without a tail and fins [Fig. 4(b)], were observed under similar experimental conditions. Although the growth mechanism for these patterns is not clear at the present stage, we think that the substrate should be responsible for their formation. Apart from this, both the strong van der Waals interactions between the tubes and the high surface density of the growing nanotubes serve as additional factors for the constituent nanotube to be "uncoiled" and allow the aligned nanotubes to develop on the quartz substrate.

In conclusion, we report the pillar-shaped fabrication and the most interesting patterns of 3D CNT alignments by pyrolysis of iron(II) phthalocyanine. The nanotube alignments have been identified as promising candidates for field emitters in applications such as flat panel displays. Moreover, we can find innumerable technical applications in the field of biomimetic materials if the ultrahydrophobic property of the pillar-shaped 3D alignments of CNTs can be transferred to artificial surfaces (*e.g.* cars, facades, foils). Further efforts should concentrate on the understanding the growth mechanism and controlled synthesis of the 3D regular arrays of the nanotubes.

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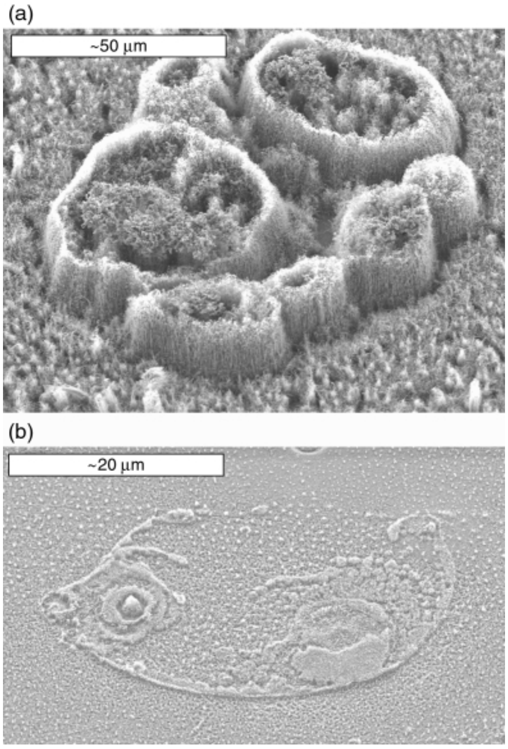

Fig. 4 SEM images of 3D nanotube patterns: (a) ring-like castles. (b) A 490 μm long crucian carp without a tail and fins.

Notes and references

1 W. A. de Heer, A. Chatelain and D. Ugarte, *Science*, 1995, **270**, 1179.
2 A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. Colbert and R. S. Smalley, *Science*, 1995, **269**, 1550.
3 Y. Chen, D. T. Show and L. Guo, *Appl. Phys. Lett.*, 2000, **76**, 2469.
4 S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell and H. Dai, *Science*, 1999, **283**, 512.
5 P. G. Collins, A. Zettle, H. Bando, A. Thess and R. E. Smalley, *Science*, 1997, **278**, 100.
6 S. J. Tans, A. R. M. Vershuerent and C. Dekker, *Nature*, 1998, **393**, 49.
7 D. Öner and T. J. McCarthy, *Langmuir*, 2000, **16**, 7777.
8 W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao and G. Wang, *Science*, 1996, **274**, 1701.
9 C. N. R. Rao, R. Sen, B. C. Satishkumar and A. Govindaraj, *Chem. Commun.*, 1998, **15**, 1525.
10 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 and D. R. M. Walton, *Nature*, 1997, **388**, 52.
11 Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal and P. N. Provencio, *Science*, 1998, **282**, 1105.
12 Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal and P. N. Provencio, *Appl. Phys. Lett.*, 1998, **73**, 3845.
13 X. B. Wang, Y. Q. Liu and D. B. Zhu, *Appl. Phys. A*, 2000, **71**, 347.
14 W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**, 1.
15 X. B. Wang, W. P. Hu, Y. Q. Liu and D. B. Zhu, *Carbon*, 2001, in press.
16 M. Terrones, P. Redlich, N. Grobert, S. Trasobares, W. Hsu, H. Terrones, Y. Zhu, J. P. Hare, C. L. Reeves, A. K. Cheetham, M. Rühle, H. W. Kroto and D. R. M. Walton, *Adv. Mater.*, 1999, **11**, 655.
17 M. Nath, B. C. Satishkumar, A. Govindaraj, C. P. Vinod and C. N. R. Rao, *Chem. Phys. Lett.*, 2000, **322**, 333.