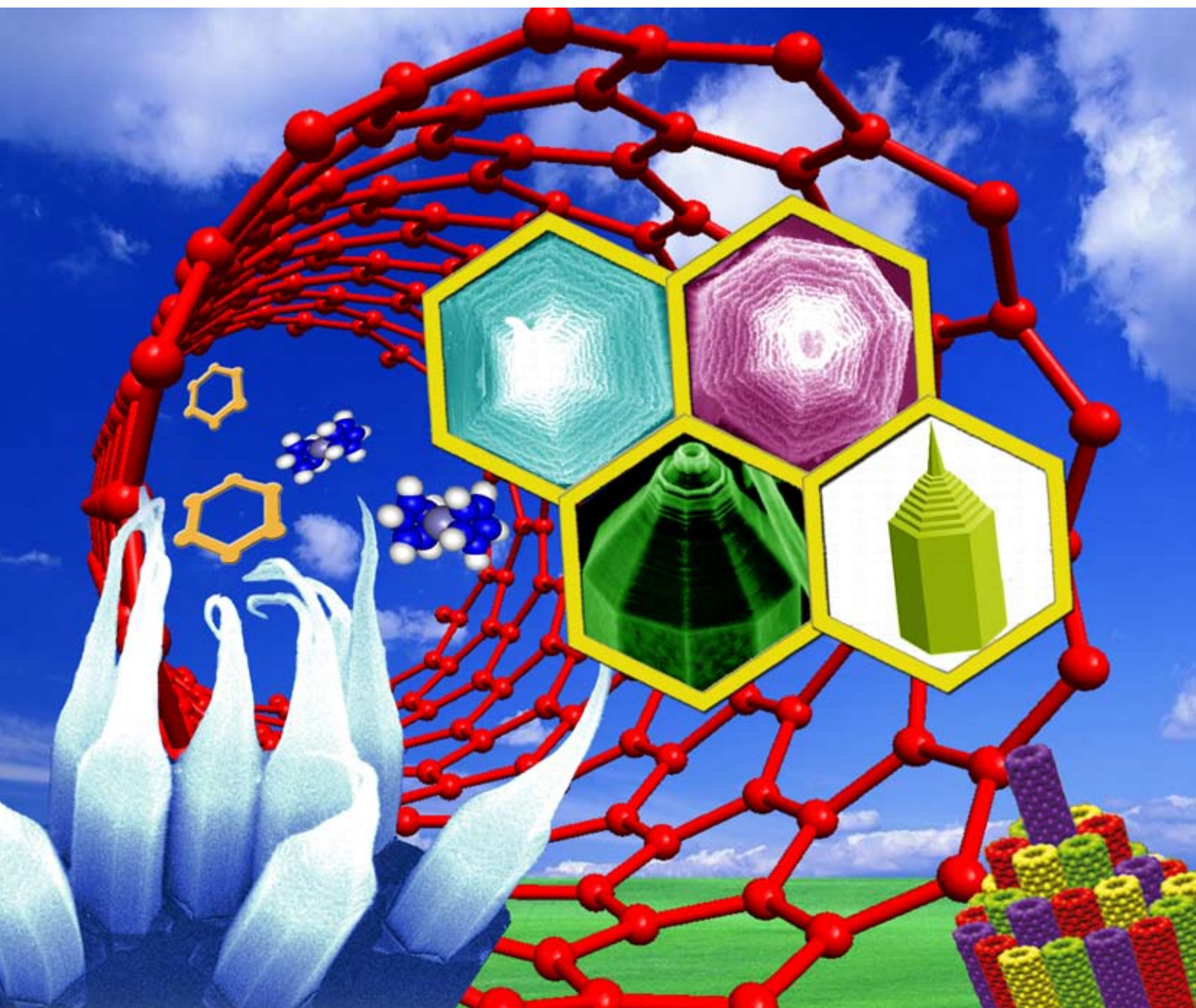


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Self-assembly of carbon nanotube polyhedrons inside microchannels†

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Well-defined carbon polyhedrons with faceted morphologies and hollow internal structures made of self-organized multi-walled carbon nanotubes have been fabricated by gas phase catalytic CVD inside microchannels, of which the confined space is critical for the formation of polyhedral structures with hexagonal, heptagonal and octagonal cross-sections that show superhydrophobic properties, with the contact angle up to 162°.

Carbon nanotubes (CNTs), with their superior electronic and physical properties, have attracted significant scientific and technological interest since their discovery.¹ The assembly of functional nano-sized CNTs into well-defined structures of controlled shape, location, orientation and density is required for many potential applications, such as field emitters, composites, chemical sensors and functional nanodevices.² Under this driving force, both *in situ* pattern growth and post-synthesis approaches have been explored for making ordered CNT architectures.^{3–6} The combination of pre-fabricated catalyst patterns with lithography and chemical vapor deposition (CVD) has resulted in highly ordered CNT patterns and networks.³ The multi-directional growth of CNTs *via* a substrate site-selective mode has been demonstrated on patterned SiO₂/Si substrates.⁴ Typical cases of post-synthesis assembly include continuous yarns and transparent sheets produced by spinning CNTs,⁵ and capillarity-induced 3D micropatterns on aligned CNT films.⁶ Nevertheless, there is still the need for facile routes to produce shape-controlled hierarchical CNT architectures.⁷

Microchannels with a range of sizes have been used widely in microfluidics and microfabrication in recent years. Each channel serves as a microreactor for the fabrication of microstructures to be used elsewhere or in-place, integrated with the other uses of microreactors. A variety of ordered structures have been fabricated in the confined spaces of microchannels using a post-synthesis approach with fluid flow, such as microelectrode arrays, patterns of colloids and strings of single-walled CNTs.⁸ Here, we report the CVD synthesis of

micro-sized carbon polyhedrons with hierarchical structures built of *in situ* self-organized CNTs inside space-confined microchannels.

The design and fabrication of the CNT-based structures involved several steps. Firstly, patterned SiO₂/Au substrates were made by conventional lithography. A 200–300 nm thick Au film was deposited on the surface of SiO₂ substrates (8 × 4 mm, 0.04 g), yielding Au patterns with a width of 200 μm; the channels between Au patterns were parallel, between which the width was 390 μm and the length was 3.5 mm, as shown in Fig. 1a. Typically, two such substrates were used for each experiment; one substrate being turned over and placed on top of the other, face-to-face, to form microchannels (Fig. 1b). Secondly, the CVD growth of CNT-based polyhedrons was performed in a two-stage furnace by exposing the sandwiched SiO₂/Au substrates to a vapor mixture of cyclohexane/ferrocene (C₆H₁₂/Fe(C₅H₅)₂). Ferrocene was placed inside a quartz boat located in the middle of the first-stage furnace, while the substrates were placed in the middle of the second-stage furnace (Fig. S1†). To avoid undesirable vaporization of ferrocene during the ramping step, the quartz tube was pulled out a little to keep the ferrocene outside of the furnace before the reaction temperature was reached (150 °C for the first furnace and 850 °C for the second). Then, cyclohexane (0.2 mL min⁻¹) was carried into the reactor with a flowing

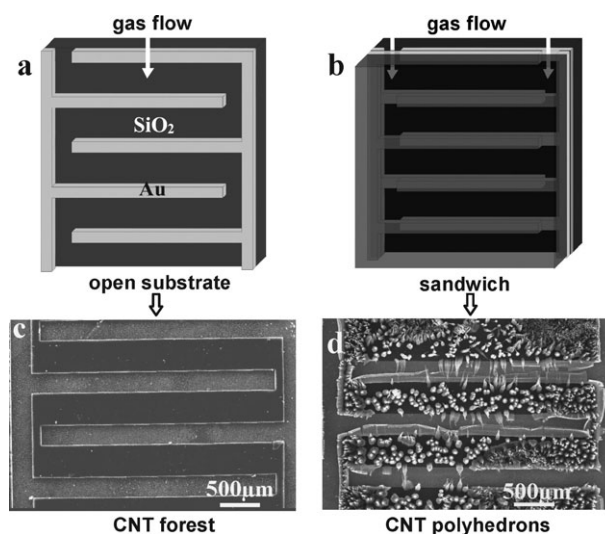


Fig. 1 Illustration of (a) an open SiO₂/Au substrate, (b) a sandwich structure made by placing two SiO₂/Au substrates face-to-face to construct microchannels between them, SEM images of (c) a CNT forest (dark) on an open substrate and (d) CNT polyhedrons on the capped substrate after CVD.

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† Electronic supplementary information (ESI) available: Schematic diagram of the experimental setup, supplementary SEM images of carbon polyhedrons and the shapes of water droplets. See DOI: 10.1039/b805622f

gas mixture of $200 \text{ mL min}^{-1} \text{ N}_2$ and H_2 ($v/v = 1 : 1$), lasting for 20 min. After the reaction, the furnaces were cooled to room temperature in an N_2 flow. The as-obtained products were examined using scanning electron microscopy (SEM, JSM-5600LV) and transmission electron microscopy (TEM, Philips Tecnai G² 20).

Fig. 1c shows that aligned CNT arrays were grown uniformly on the patterned SiO_2 surface of the open substrate in high density, and no CNTs were observed on the Au film that was commonly used as a mask to prevent the growth of CNTs at pre-defined positions.⁹ Interestingly, when capped substrates were used instead of the open one under identical conditions, the growth style of CNTs on the SiO_2 surface changed remarkably. It was found that localized growth occurred inside the channels on both the top and bottom surfaces of the sandwich substrate, which differed from the uniformly distributed CNT forest obtained on the open substrate (Fig. 1d and Fig. S2[†]). High magnification SEM and TEM examination revealed that these micro-sized assemblies were well-defined polyhedral structures (Fig. 2), consisting of multi-walled CNTs with diameters of 30–50 nm (Fig. 3).

The polyhedrons formed *via in situ* CNT assembly inside the microchannels have 6–8 facets, and their morphologies are very similar to polyhedral graphite crystals.¹⁰ They are short columns of up to $100 \mu\text{m}$ height and $50\text{--}100 \mu\text{m}$ diameter. Fig. 2a shows some well-developed pencil-like polyhedrons of about $70 \mu\text{m}$ height and $50 \mu\text{m}$ diameter, ending with a long tail comprising of CNT bundles. The fact that their height exceeds that of the channel indicates that growing CNTs are able to lift the upper plate. It can also be seen that the CNT polyhedrons have a tendency to aggregate, *i.e.* two or more of them can associate together closely, and in some cases can share the same surface or facet, as shown in Fig. 2b. A magnified SEM image of a well-developed CNT hexagon with nearly identical facets is shown in Fig. 2c. A hexagonal CNT dome without a column, similar in morphology to polygonized carbon cones,¹¹ is shown in Fig. 2d. The facets and steps can

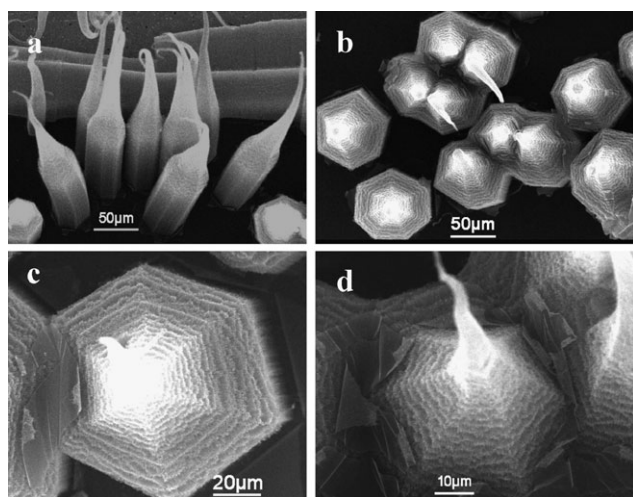


Fig. 2 (a, b) SEM images of typical CNT polyhedrons with varying heights, diameters and facets inside different channels. High magnification SEM images of (c) a well-defined hexagonal CNT polyhedron and (d) a dome.

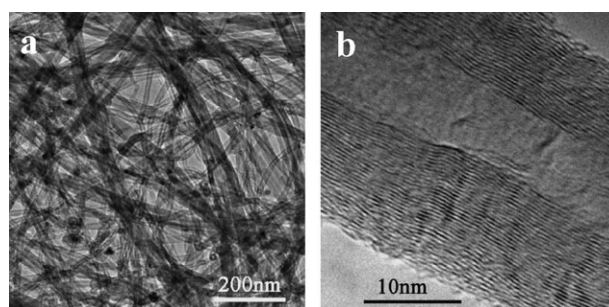


Fig. 3 (a) TEM image of CNTs that act as building components of the polyhedrons and (b) a typical HRTEM image showing that they are graphitized multi-walled CNTs.

be clearly seen on the surface of the domes in Fig. 2c and 2d, indicating a layer-by-layer growth process. It has been found that the average diameter and height of the CNT polyhedrons are fairly uniform within the same channel (Fig. 2a and 2b); however, the average diameter increases and the height of columns decreases away from the gas inlet, which may be due to a decreasing supply of active reactants (Fig. S3[†]).

Typically, the polyhedral structures terminate with thin protruding tails of CNT bundles, which can be removed from the polyhedrons (Fig. 4a), indicating a weak adherence between the tail and the dome. The removal of a tail reveals a hollow structure inside the dome (inset in Fig. 4a). Hollow structures are also observed at the bottom of the polyhedrons

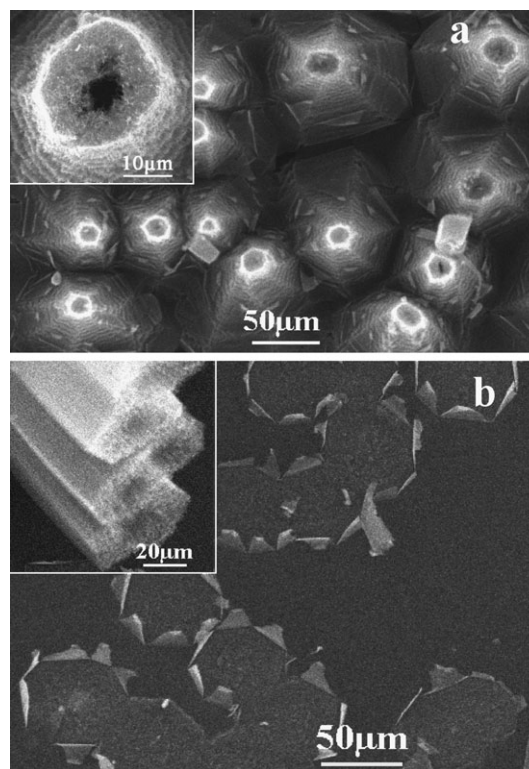


Fig. 4 SEM images of (a) hollow domes of CNT polyhedrons obtained by removing the tails (inset shows magnified image of an individual hollow dome) and (b) footprints left on the substrate after the removal of CNT polyhedrons (inset shows the bottoms of hollow CNT polyhedrons removed from the substrate).

(see inset in Fig. 4b) after their removal from the substrate using tweezers. These observations suggest that the polyhedrons are hollow tube-like structures, with their tops closed-off by faceted domes. Polyhedron removal leaves behind footprints that delineate the distribution of CNTs (Fig. 4b), indicating their highly selective nucleation on the substrate.

The confined microspaces between rigid substrates are obviously critical for the formation and growth of well-defined CNT polyhedrons, because aligned CNT forests were obtained when open substrates were used under the same conditions (Fig. 1a and 1c). It is well-known that the position of each CNT grown on the substrate surface is determined by the corresponding catalyst nanoparticle; therefore the formation of CNT polyhedrons can be traced back to the organization of catalyst nanoparticles on the substrate during the initial stages. It is assumed that several steps are involved in the process, including the dissociation of catalyst precursor, catalyst clustering to form nanoparticles (which subsequently self-organize to form patterns on the substrate in the confined micro-spaces) and the initiation of CNT growth on the catalysts. It has been well-documented that the self-assembly of pre-synthesized monodispersed nanocrystals over a long distance in liquid films can lead to various mesostructures, such as polygonal networks and rings, due to thermocapillary flow during evaporation.¹² Similar phenomena are also observed here for *in situ* formed catalyst nanoparticles during the CVD growth of CNTs inside microchannels, suggesting that the catalyst is deposited in a liquid state on the SiO₂ substrate. A detailed examination of the dome (Fig. 2c and 2d) shows that the morphology evolved initially *via* a layer-by-layer growth scheme,¹³ expanding from the center to the fringe. During this process, CNTs in the central part were lifted from the substrate (Fig. S4†) due to strong van der Waals interactions between CNTs, and relatively weak bonding between CNTs and the substrate. The easy removal of the CNTs from the dome provides essential evidence for this assumption. In later stages, the sandwich-like substrates eventually broke open due to the mechanical energy of the growing CNTs¹⁴ (Fig. S5†), and the confining effect of the channels (which was observed during the initial stages) vanished. Thus, a prolonged growth time only affected the height of the CNT polyhedrons, without there being any further change to their cross-section (Fig. 2a). The coexistence of well-grown CNT polyhedrons and shorter columns, or even semi-domes, inside different channels further suggests that the faceted domes are formed prior to the columns, implying a base growth process (Fig. S4†). To some degree, this is reminiscent of the well-known base growth of CNTs.¹⁵

In summary, we have reported a novel approach to micro-sized CNT polyhedron architectures. The self-organization of CNTs into polyhedra produces superhydrophobic films with contact angles of over 160° (Fig. S6†), which are attractive for nanofluidic applications. These CNT-based polyhedrons may have potential applications in composites, catalysis and fluidic separation.

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Notes and references

- (a) S. Iijima, *Nature*, 1991, **354**, 56; (b) W. A. de Heer, A. Chatelain and D. Ugarte, *Science*, 1995, **270**, 1179; (c) *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, ed. M. S. Dresselhaus, G. Dresselhaus and P. Avouris, Springer-Verlag, Berlin, 2001; (d) S. C. Tsang, P. J. F. Harris and M. L. H. Green, *Nature*, 1993, **362**, 520.
- (a) 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; (b) 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; (c) S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Cassell and H. J. Dai, *Science*, 1999, **283**, 512; (d) B. J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas and L. G. Bachas, *Science*, 2004, **303**, 62; (e) P. J. F. Harris, *Int. Mater. Rev.*, 2004, **49**, 31; (f) Y. Xu, E. Flor, M. J. Kim, B. Hamadani, H. Schmidt, R. E. Smalley and R. H. Hauge, *J. Am. Chem. Soc.*, 2006, **128**, 6560.
- (a) H. J. Dai, *Acc. Chem. Res.*, 2002, **35**, 1035; (b) S. Huang, L. Dai and A. W. H. Mau, *Adv. Mater.*, 2002, **14**, 1140.
- B. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath and P. M. Ajayan, *Nature*, 2002, **416**, 495.
- (a) K. Jiang, Q. Li and S. Fan, *Nature*, 2002, **419**, 801; (b) Y. Li, I. A. Kinloch and A. H. Windle, *Science*, 2004, **304**, 276; (c) M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson and R. H. Baughman, *Science*, 2005, **309**, 1215.
- (a) H. Liu, S. Li, J. Zhai, H. Li, Q. Zheng, L. Jiang and D. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 1146; (b) N. Chakrapani, B. Wei, A. Carrillo, P. M. Ajayan and R. S. Kane, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 4009.
- (a) Z. Zhao, J. Qu, J. Qiu, X. Wang and Z. Wang, *Chem. Commun.*, 2006, **6**, 594; (b) Y. Yan, M. B. Chan-Park and Q. Zhang, *Small*, 2007, **3**, 24.
- (a) P. A. Kenis, R. F. Ismagilov, S. Takayama, G. M. Whitesides, S. Li and H. S. White, *Acc. Chem. Res.*, 2000, **33**, 841; (b) P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides and G. D. Stucky, *Science*, 1998, **282**, 2244; (c) Y. Yin, Y. Lu, B. Gates and Y. Xia, *J. Am. Chem. Soc.*, 2001, **123**, 8718; (d) Y. Huang, X. Duan, Q. Wei and C. M. Lieber, *Science*, 2001, **291**, 630; (e) J. Chen and W. A. Weimer, *J. Am. Chem. Soc.*, 2002, **124**, 758.
- A. Cao, R. Baskaran, M. J. Frederick, K. Turner, P. M. Ajayan and G. Ramanath, *Adv. Mater.*, 2003, **15**, 1105.
- (a) Y. Gogotsi, J. A. Libera, N. Kalashnikov and M. Yoshimura, *Science*, 2000, **290**, 317; (b) P. H. Tan, S. Dimovski and Y. Gogotsi, *Philos. Trans. R. Soc. London, Ser. A*, 2004, **362**, 2289.
- (a) S. Dimovski and Y. Gogotsi, Graphite Whiskers, Cones and Polyhedral Crystals, in *Nanomaterials Handbook*, ed. Y. Gogotsi, CRC Press, Boca Raton, 2006, pp. 175–200; (b) G. Zhang, X. Jiang and E. Wang, *Science*, 2003, **300**, 472.
- (a) P. C. Ohara and W. M. Gelbart, *Langmuir*, 1998, **14**, 3418; (b) U. Thiele, M. Mertig and W. Pompe, *Phys. Rev. Lett.*, 1998, **80**, 2869; (c) C. Stowell and B. A. Korgel, *Nano Lett.*, 2001, **1**, 595; (d) M. Maillard, L. Motte and M. P. Pileni, *Adv. Mater.*, 2001, **13**, 200.
- (a) X. Li, A. Cao, Y. J. Jung, R. Vajtai and P. M. Ajayan, *Nano Lett.*, 2005, **5**, 1997; (b) M. Pinault, V. Pichot, H. Khodja, P. Launois, C. Reynaud and M. Mayne-L'Hermite, *Nano Lett.*, 2005, **5**, 2394.
- A. J. Hart and A. H. Slocum, *Nano Lett.*, 2006, **6**, 1254.
- (a) G. G. Tibbetts, M. G. Devour and E. J. Rodda, *Carbon*, 1987, **25**, 367; (b) R. T. K. Baker, *Carbon*, 1989, **27**, 315; (c) Y. Saito, M. Okuda, N. Fujimoto, T. Yoshikawa, M. Tomita and T. Hayashi, *Jpn. J. Appl. Phys., Part 2*, 1994, **33**, L526; (d) K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura and S. Iijima, *Science*, 2004, **306**, 1362.