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3D Silicon oxide nanostructures: from nanoflowers to radiolaria

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Novel flower-like nanostructures consisting of silicon oxide nanofibers, radially attached to a single catalytic particle, were generated by solid–solid and gas–solid reactions under a temperature gradient. In this process, a mixture of SiC and Co powders, deposited on silica substrates and heated under an Ar/CO atmosphere at *ca.* 1500 °C, produced material with unusual three-dimensional (3D) networks of nanofibers of uniform diameter (*ca.* 20–120 nm) and length (*ca.* 10–250 µm). Scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray powder diffraction and energy dispersive X-ray (EDX) analyses reveal that the nanofibres are amorphous and consist only of silicon oxide, generated from the reaction of CO with SiC. Nanostructure formation is catalyzed by Co particles, which act as nucleation sites and templates for 3D growth. Experiments using Si_3N_4 and Si in conjunction with other catalysts (*e.g.* Fe, Ni and CoO) yield similar results and confirm that the resulting SiO_x fibres display virtually unique and remarkable radial growth starting from single metal particles. These structures exhibit morphologies comparable to radiolarian and diatom skeletons and may provide insight into the formation of microbiological systems.

Introduction

Nanomaterials research continues to accelerate and, as a consequence, novel structures with remarkable mechanical and transport properties have recently been developed.[1–6] In particular, the synthesis of tube-like nanostructures with stoichiometric compositions: C,[7] BC_3,[8] BC_2N,[9] BCN,[9,10] BN,[11,12] MoS_2,[13] and WS_2,[14] and wire-like nanomaterials (*e.g.* C nanofibres,[15] SiC,[16] and GaN[17] nanorods, Sn[18] nanowires *etc.*), has led to a revolution in nanotechnology. Preliminary studies of some of these one-dimensional nanostructures indicate that they may find use as microscope probes,[19] field emission sources,[20] gas storage materials,[21] and semiconducting materials.[22] As a consequence of the discovery of these exciting structures, numerous growth mechanisms,[23] and alternative routes to novel nanomaterials, have been proposed.[24–30] For instance, the synthesis of crystalline Si and Ge semiconducting nanowires,[31,32] may lead to improved electrical and optical devices, although this goal has proved difficult to achieve.[33] Alternative methods such as template-mediated processes using carbon nanotubes or zeolites[34,35] can provide a measure of controlled growth but, in general, polycrystalline nanostructures result.

In this paper, we describe the generation of novel nanostructures by heating SiC, deposited on a silica substrate, in the presence of Co powder. The resulting flower-like structures are composed of silicon oxide, and appear to have grown by a gas–solid phase reaction involving CO, catalysed by the Co particles. These structures may prove to be useful as three-dimensional composite materials and as novel catalytic supports.

Experimental

A 1 : 1 (by weight) mixture of SiC (Goodfellow Ltd., 99.9% purity, 400 mesh) and Co (325 mesh) was dispersed by sonication in acetone, and the resulting suspension was transferred by pipette on to a silica plate (10 × 5 × 1 mm). The acetone was allowed to evaporate leaving a uniform grey film (*ca.* 0.5 mm thick). The plate was then placed on a graphite heater (50 × 5 × 0.3 mm) under an Ar and/or CO atmosphere (400 Torr, Fig. 1), and a dc (30–50 A) was applied until the heater reached *ca.* 1500 °C (measured by optical pyrometry). During 60 min heating, the original grey film became lighter. After removing the substrate from the heater, the presence of a yellow–green powder was observed on top of the graphite heater, and the undersurface of the silica substrate became rough. After the experiment a color change on the reaction chamber wall was noticed, possibly due to the deposition and/or sublimation of byproducts. Further experiments were also carried out using mixed films: Si/Co, Si_3N_4/Co, SiC/CoO and SiC/Fe. In addition, an interesting material, so-called ‘bamboo-milk’, a naturally occurring form of SiO_2 containing *ca.* 2–3% Fe by weight, was also employed as a starting material in some supplementary experiments.

The resulting film samples were analyzed directly by scanning electron microscopy (SEM; coated with gold for 4 min; Leo 5420 operated at 10–20 keV), transmission electron microscopy (TEM; H-7100 operated at 120 keV, JEM-2010 operated at 200 keV, JEM-4000 operated at 400 keV), energy dispersive X-ray (EDX; using a Noran Instruments detector

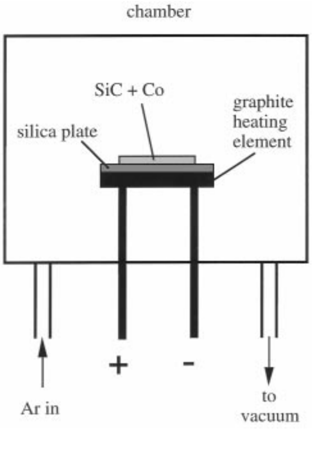

Fig. 1 Furnace assembly

attached to the JEM-2010) analysis, and X-ray powder diffraction (Siemens D-5000, Cu-Kα radiation).

Results and Discussion

An SEM image of the substrate, prior to heating, is shown in Fig. 2(a). After heating, SEM images reveal the presence of large quantities of flower-like branched nanostructures (networks) radiating from spheres [*ca.* 0.5–1 μm diameter, Fig. 2(b)], exhibiting a pronounced 3D feature [Fig. 2(c)]. These branches possess smooth surfaces, are—for a given batch—of uniform diameter (20–120 nm) and length (10–250 μm), and sometimes split into two or three sub-branches [Fig. 2(d)]. A TEM study also verifies nanostructures consisting of radially attached fibres [Fig. 3(a)]. In rare instances, TEM observations of the branches reveal the existence of loops [Fig. 3(b)]. A round Co particle is shown in Fig. 3(c). Further HRTEM examination shows that the fibres are amorphous [Fig. 3(d)] and EDX analyses indicate that they consist solely of silicon and oxygen [Fig. 4(a)], while the central spherical particle is metallic Co [Fig. 4(b)]. An X-ray powder diffraction study of the heated sample showed the presence of SiO_2, SiO and intermediate phases SiO_x ($x = 1$–2), SiC residues, in addition to Co and its oxides (*e.g.* Co_2O_3 and CoO) as minor constituents. These nanofibers appear to consist only of silicon oxides.

This striking result poses many questions about silicon oxide nanoflower formation. For example, SiC melts at *ca.* 2830 °C at ambient pressure and, when sintered, can be handled without decomposition, up to 1800 °C in air. It is unlikely that SiC oxidizes under our experimental conditions. Indeed heating silica alone does not result in the flowers. It appears that the graphite heater reacts with the underside of the silica substrate to form β-SiC (yellow–green powder; revealed by XRD measurements). There are still some questions about the mechanism of formation of these remarkable structures. However we here advance a plausible partial explanation of these results involving a possible reaction between the heater and silica substrate

$$3C + SiO_2 \xrightarrow{\text{heat}} SiC + 2CO \qquad (1)$$

leading to the formation of solid SiC and *in situ* liberation of CO. The CO then immediately reacts with the SiC/Co film, at an unspecified temperature

$$SiC + CO \xrightarrow[\text{heat}]{\text{Co}} SiO + 2C \qquad (2)$$

catalysed by Co, generating silicon oxide and additional nanofibers. SEM observation of the heated silica substrates reveals the existence of deep fissures embedded in the substrate [Fig. 5(a)], which we believe enables CO to diffuse through the substrate, thus reaching and reacting with the SiC/Co film. The resulting SiO [byproduct in reaction (2)], agglomerates [sometimes around Co particles; Fig. 6(a) and (b)] and forms the nanofibers [Fig. 6(c)]. Carbon may have been removed as a semi-volatile impurity as there are carbonaceous deposits on the chamber walls after reaction. It seems that the generation of nanofibers involves solid (S)–solid (S) [reaction (1)] and gas (G)–solid (S) [reaction (2)] processes.

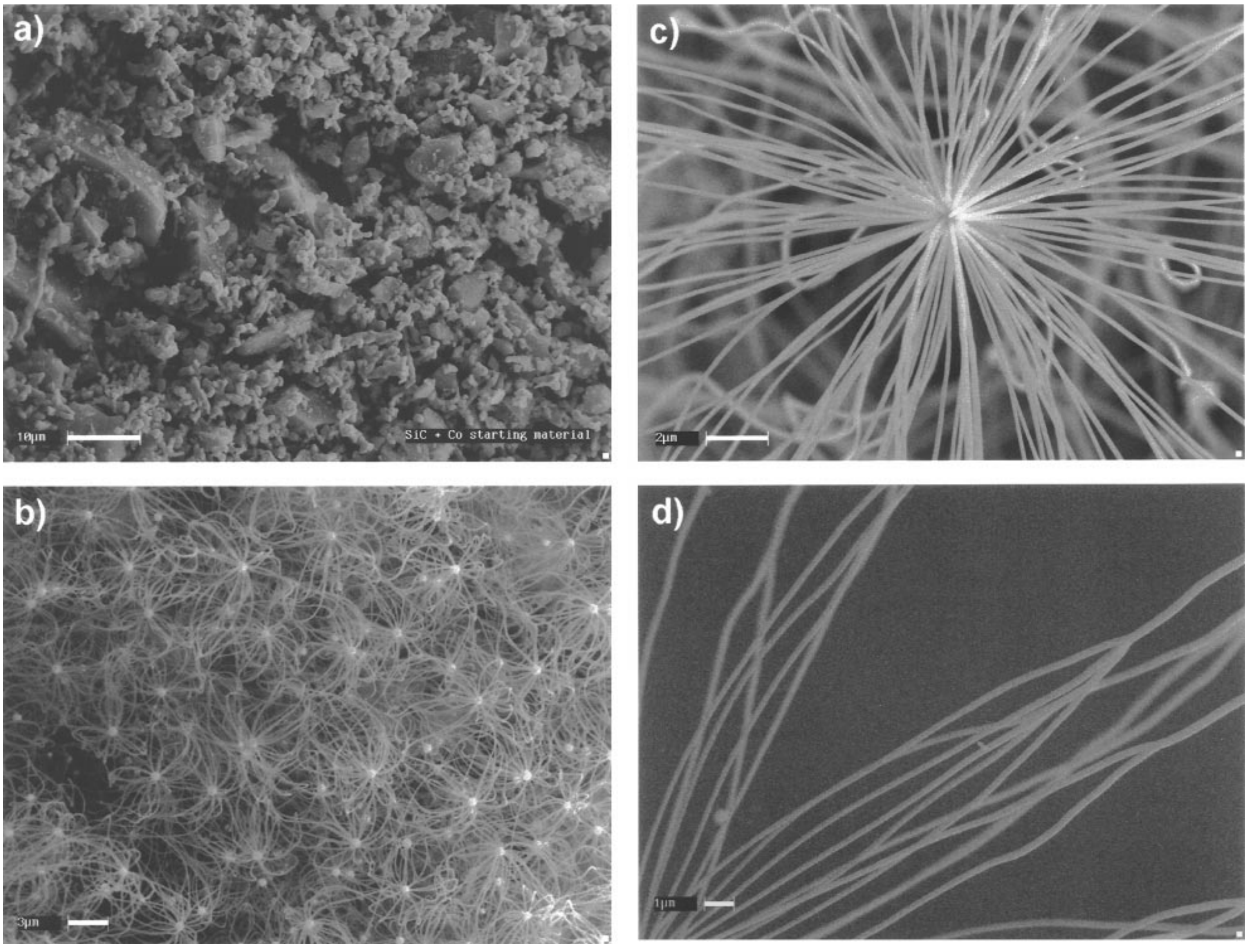

Fig. 2 SEM images. (a) before heating; large SiC particles covered by a fine Co powder. (b) After heating; sample surface covered by flower-like nanofibers. (c) A typical three-dimensional feature radiating from a central spherical Co particle. (d) Branched nanofibers emanating from the central particle (location: bottom left).

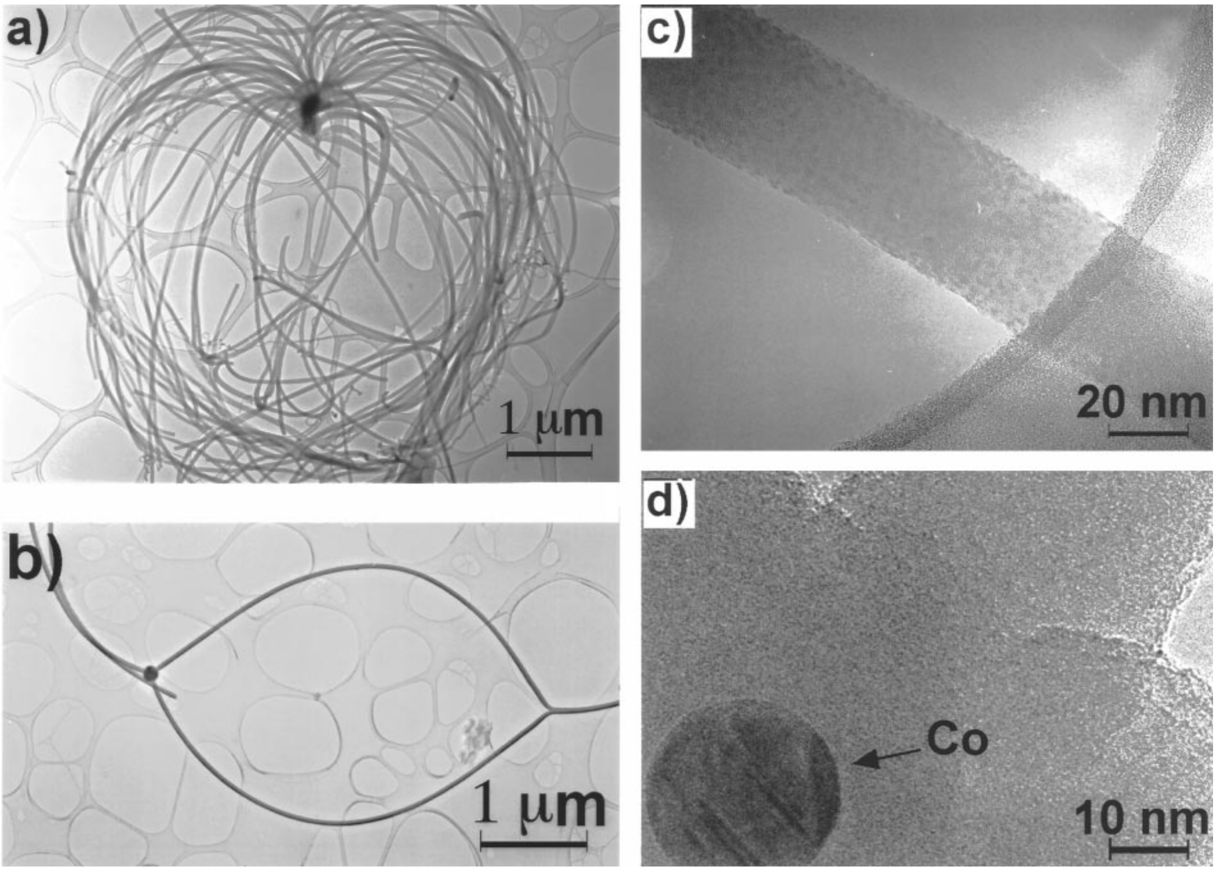

Fig. 3 (a) A 3D nanoflower under TEM, illustrating the connection between the nanofibers and the central particle (after 5 min sonication). (b) A closed loop. (c) HRTEM image: non-crystalline fibres. (d) A typically spherical Co particle (surrounded by silicon oxide) responsible for the radial nanofiber growth.

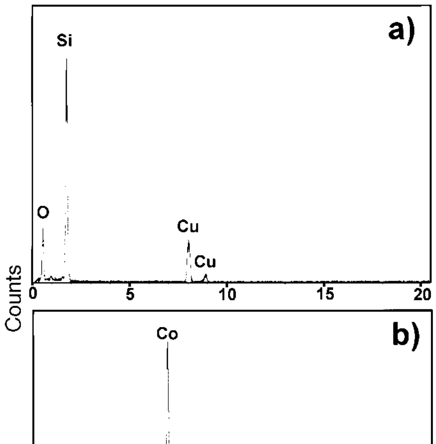

Fig. 4 EDX measurements: (a) a typical nanofiber, containing oxygen (*ca.* 0.516 keV Kα) and silicon (*ca.* 1.744 keV Kα); (b) central core particles containing only Co (*ca.* 6.920, 0.778 keV, Kα_1 and Lα_1, respectively). The Cu signals arise from the TEM sample holder (*ca.* 8.024 and 8.914 keV).

Additional experimental evidence supports this conjecture. For example, when the graphite heater was replaced by a tungsten heater, no reaction took place at the tungsten/silica substrate interface (*i.e.* no CO was produced) at *ca.* 1500 °C, and the grey film (SiC/Co) remained unchanged [reaction (1) did not occur]. When a graphite heater was employed in the absence of Co (catalyst), nanoflowers were not observed. Finally, when the graphite heater was activated in the presence of a pure Co powder film, nanostructures were not formed on the silica substrate [reaction (2) did not happen].

Experiments using silicon powder (Aldrich, 325 mesh, 99% purity) mixed with Co, also lead to flower-like nanostructures (as did Si_3N_4/Co; SiC/CoO, SiC/Fe and SiC/Ni). These results suggest that the catalysts and the *in situ* generated CO [arising from the reaction between the carbon heater and the silica plate (S–S)], are crucial for the production of silicon oxide nanofibers/nanoflowers (G–S).

In order to provide support for the intervention of CO, we performed additional experiments. A tungsten heater and a pure Si substrate were used to avoid reaction (1) and CO gas was passed directly into the chamber (*ca.* 400 Torr) in order to react with the SiC [reaction (2)]. All other parameters (catalyst, temperature and time) were kept constant. SEM and HRTEM observations of the products revealed the formation of nanoflowers. This result, reaction (2), provides strong evidence for a key role in the process.

The catalytic effect of Co particles in allied experiments, involving gas-phase processes, for the formation of carbon nanotube/nanofiber and other nanostructures, has been widely studied.[23] For silicon oxide nanoflower formation, it is likely that Co particles agglomerate, reduce their surface energy, and form larger spherical particles at temperatures close to the melting point of Co (1495 °C). The silicon oxide formed during reactions (1) and (2) diffuses directly through or is deposited on the Co particles. These particles, covered by SiO, act as nucleation sites for fiber growth, and seem to be located at the growing ends during nanoflower formation [Fig. 5(b)]. In this process, the agglomerated Co particles (possibly the central nanoflower cores) will continuously reduce their size, as a

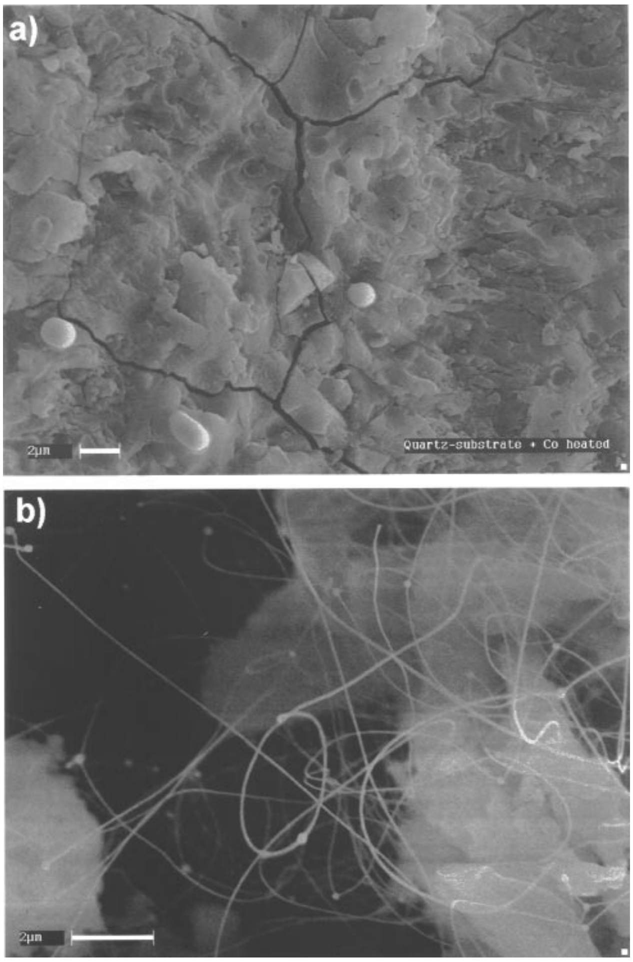

Fig. 5 (a) Fissures in the heated silica substrate; (b) Co particles at the fiber tips

result of the generation of more and more growing arms. Therefore, Co particles are vital for axial nanofibre growth and the formation of flower-like nanostructures. Empirical observations suggest that the number of the arms and the size of the central particles within the nanoflowers are intimately related. For instance, from a comparison of Fig. 2(b) and (c) it appears that as the size of the central core decreases, the more radially grown nanofibres emerge. HRTEM observations confirm that the single spherical particles, located at the radial centers of the nanoflowers and surrounded by silicon oxide, consist of metallic Co [Fig. 3(c)]. It is important to note that the temperature gradient and electrostatic effects within the reacting film may also play a key role in this process.

At this stage it is fair to say that we have not arrived at a totally consistent overall scenario that can compellingly explain the creation of these remarkably elegant structures. However on the basis of the extensive series of experiments carried out to date, we propose the following as a plausible partial explanation of the observations. Nevertheless, difficulties still remain which we shall highlight. It is clear that further experiments are needed and these are currently being carried out in an attempt to improve our understanding. We believe our observations to be of sufficient interest to report them at this stage.

The original aim of the experiments was to study the possible ways in which carbon might separate from SiC when heated in the presence of a Co catalyst. Thus SiC and Co were mixed, spread over a silica substrate, and heated. As a result, nanoflowers (Fig. 2 and 3) were formed. The initial assumption that the limbs of the nanoflowers were carbon nanotubes was soon confounded by the analytical results which showed them to consist of SiO_x. On the basis of these results, we suggest a plausible growth mechanism for these nanoflower-like structures, involving a Co catalytic template model depicted schematically in Fig. 7.

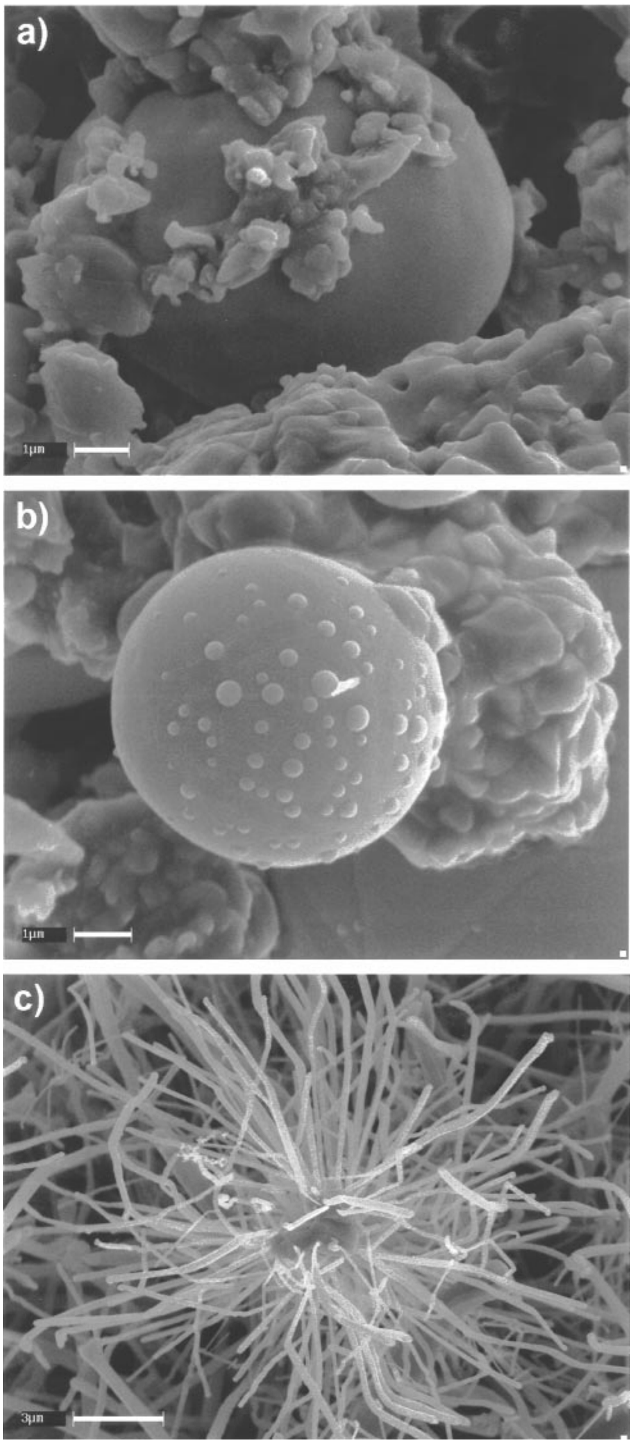

Fig. 6 SEM images. (a) Smooth spherical Co particles with minimal surface energy. (b) Surface blisters. (c) Nanofibers radiating from the blistered surface

The ability of Co to create such stalks is supported by an ancillary study, using 'bamboo-milk', shown in Fig. 8(a) and (b). Here we see several remarkable structures. Most interesting is one (arrowed) which appears to grow out of a crater. This indicates that a Co particle can reorganise a fluid globule of silica into a stalk. We think that a similar process is occurring in the main experiment, because SiO_x is produced at the interface between SiC/Co/CO and thus SiO_x is continuously being formed by the SiC/CO reaction. The stalks [Fig. 8(a)

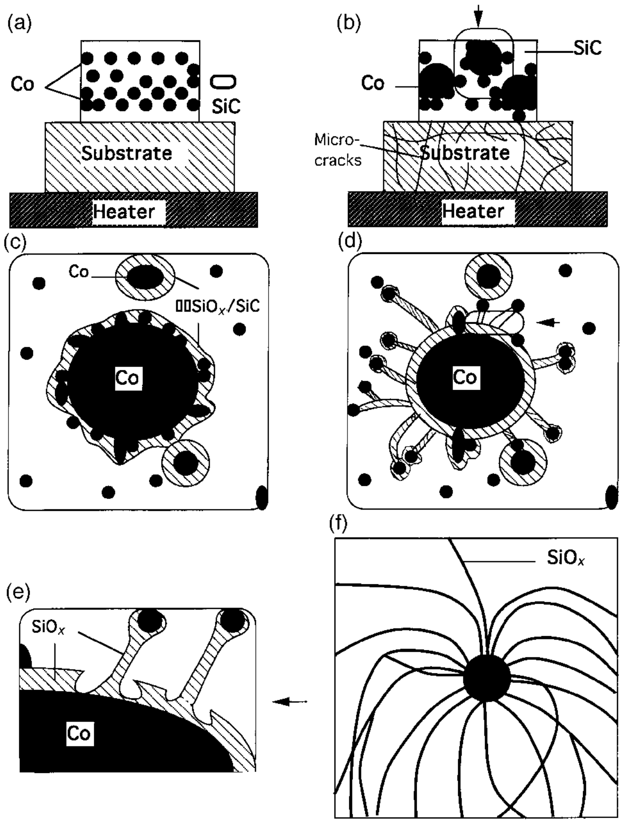

Fig. 7 Nanoflower growth model: (a) heating assembly; (b) fissured SiO_2 and agglomerated Co; (c) spherical Co particles; (d) initial growth stage; (e) magnified nanotube growth; (f) final stages of growth

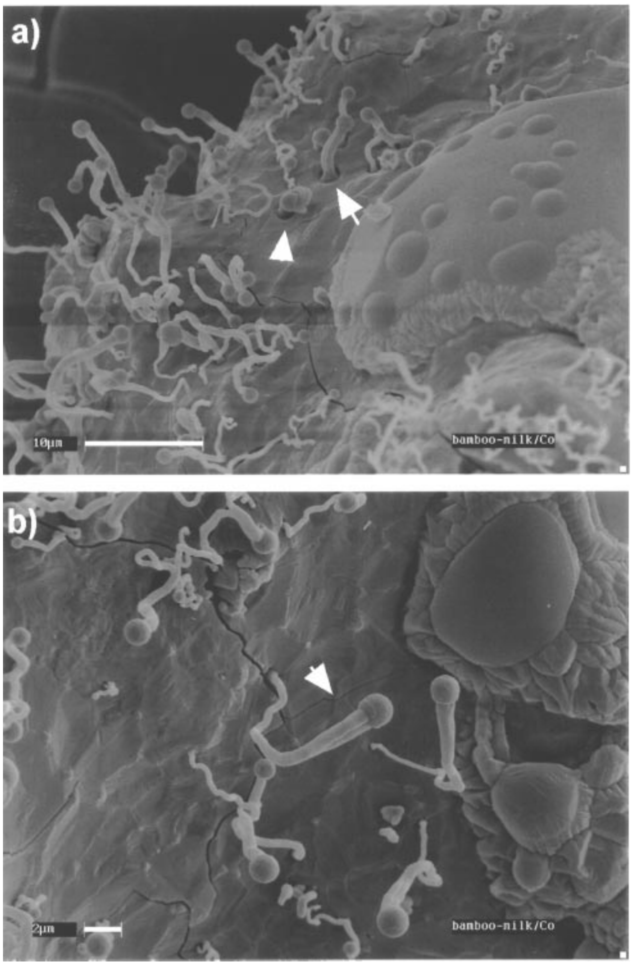

Fig. 8 Bamboo-milk SEM images. (a) Initial stages of Co-catalysed fiber growth from the blisters; (b) fiber growth (with splitting) from the fissures.

and (b)] are short, perhaps because, in this experiment, only a small amount of restructurable SiO_x is available at the Co/SiO_x interface, whereas in the SiC/Co/CO system it is being continuously generated. Several questions still remain, not least of which is the destination of the carbon which is the secondary product of the process we postulate in eqn. (2). A dark apparently carbonaceous deposit, observed on the walls of the thermolysis chamber, may provide an explanation. It may indicate that semi-volatile carbonaceous material has formed by the reaction of carbon with impurities such as hydrogen that invariably remain in even the best samples of graphitic carbon.

Particularly interesting is the bifurcation, observed in Fig. 8(b). This indicates that a single Co particle can cause a splitting to produce two (or more) stalks. This capability accounts for the split structure [Fig. 3(b)] which is closed by a particle at the other end of the loop. The structures at the interface between the stalks and the particle are most revealing. We are currently studying related systems in an attempt to elucidate the mechanism which gives rise to these interesting structures.

Conclusions

Elegant novel flower-like SiO_x ($x=1$–2)/Co nanostructures have been prepared by a solid phase or gas/solid reaction, resulting in growth from spherical template catalytic particles. This simple and controllable method may now facilitate *in situ* monitoring of nanofibre growth. The 3D features associated with these nanoflowers may prove useful in reinforcing composite materials or in further modifying other nanostructures.

We note here interesting morphological similarities between the flower-like structures and the skeletons of radiolaria and diatoms. Radiolaria consist of single-cell creatures (zooplankton) related to amoebae that inhabit silicon oxide shells possessing long radial spines. They are ancient life forms which have existed in the oceans for millions of years. These skeletons are formed *via* a biomineralization process,[36] which involves secretion of amorphous silica. The creatures may possess various morphologies depending upon many factors, such as sea temperature and salinity.[37] There are interesting similarities between our abiotic structures and the skeletons of the creatures, suggesting the possibility of a mechanistic connection which may merit further investigation.

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References

1 M. R. Falvo, G. J. Clary, M. R. Taylor II, V. Chi, F. P. Brooks Jr., S. Washburn and R. Superfine, *Nature* (*London*), 1997, **389**, 582.
2 C. E. Wong, P. E. Sheehan and C. M. Lieber, *Science,* 1997, **277**, 1971.
3 B. I. Yakobson and R. E. Smalley, *Am. Sci.*, 1997, **85**, 324.
4 M. M. Treacy, T. M. Ebbesen and J. M. Gibson, *Nature* (*London*), 1996, **381**, 678.
5 P. G. Collins, A. Zettl, H. Bando, A. Thess and R. E. Smalley, *Science,* 1997, **278**, 100.
6 F. F. Fan and A. J. Bard, *Science,* 1997, **277**, 1791.
7 S. Ijima, *Nature* (*London*), 1991, **354**, 56.

8 Z. Wengsieh, K. Cherrey, N. G. Chopra, X. Blase, Y. Miyamoto, A. Rubio, M. L. Cohen, S. G. Louie, A. Zettl and R. Gronsky, *Phys. Rev. B*, 1995, **51**, 11299.

9 O. Stephan, P. M. Ajayan, C. Colliex, P. Redlich, J. M. Lambert, P. Bernier and P. Lefin, *Science,* 1994, **266**, 1683.

10 M. Terrones, A. M. Benito, C. Manteco-Diego, W. K. Hsu, O. I. Osman, J. P. Hare, D. G. Reid, H. Terrones, A. K. Cheetham, K. Prassides, H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1996, **257**, 576.

11 M. Terrones, W. K. Hsu, H. Terrones, J. P. Zhang, S. Romas, J. P. Hare, R. Castillo, K. Prassides, A. K. Cheetham, H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1996, **259**, 568.

12 N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, *Science*, 1995, **269**, 966.

13 L. Margulis, G. Salitra, R. Tenne and M. Talianke, *Nature* (*London*), 1993, **365**, 113.

14 R. Tenne, L. Margulis, M. Genut and G. Hodes, *Nature* (*London*), 1992, **360**, 444

15 M. Endo, *CHEMTECH*, 1988, **18**, 568.

16 H. Dai, E. W. Wong, Y. Z. Lu, S. Fan and C. M. Lieber, *Nature* (*London*), 1995, **375**, 769.

17 W. Han, S. Fan, Q. Li and Y. Hu, *Science*, 1997, **277**, 1287.

18 W. K. Hsu, M. Terrones, H. Terrones, N. Grobert, A. I. Kirkland, J. P. Hare, K. Prassides, P. D. Townsend, H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1998, **284**,177.

19 H. Dai, J. Halner, A. G. Reizler, D. T. Colbert and R. E. Smalley, *Nature* (*London*), 1996, **384**, 147.

20 Y. Saito, K. Hamaguchi, K. Hata, K. Uchita, Y. Tasaka, Y. Ikazaki, M. Yamura, A. Kasuya and Y. Nishina, *Nature* (*London*), 1997, **389**, 554.

21 G. E. Gadd, M. Blackford, S. Moricca, N. Webb, J. P. Evans, A. M. Smith, G. Jacobsen, S. Leung, A. Gay and Q. Hua, *Science*, 1997, **277**, 933.

22 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of fullerenes and carbon nanotubes*, Academic, San Diego, 1996.

23 T. W. Ebbesen and P. M. Ajayan, *Nature* (*London*), 1992, **358**, 220.

24 X. K. Wang, X. W. Lin, M. Mesleh, M. F. Jarrold, V. P. Dravid, J. B. Ketterson and R. P. H. Chang, *J. Mater. Res.*, 1995, **10**, 1977.

25 S. Iijima and T. Ichihashi, *Nature* (*London*), 1993, **363**, 603.

26 M. T. Yacaman, M. M. Yoshida and L. Rendon, *App. Phys. Lett.*, 1993, **62**, 202.

27 M. Ge and K. Sattler, *Science*, 1993, **260**, 515.

28 W. K. Hsu, J. P. Hare, M. Terrones, H. W. Kroto, D. R. M. Walton and P. J. F. Harris, *Nature* (*London*), 1995, **377**, 687.

29 W. K. Hsu, M. Terrones, J. P. Hare, H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1996, **262**, 161.

30 D. S. Bethune, C. H. Kiang, M. S. Deveries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Nature* (*London*), 1993, **363**, 605.

31 G. D. Saunders and Y. C. Chang, *Phys. Rev. B*, 1992, **45**, 9202.

32 L. E. Brus, *J. Phys. Chem.*, 1994, **98**, 3575.

33 A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.

34 C. R. Martin, *Science*, 1994, **266**, 1961.

35 C. G. Wu and T. Bein, *Science*, 1994, **266**, 1013.

36 S. Mann, *Nature* (*London*), 1993, **365**, 499.

37 D. Berger, *Journeys in the microspace*; *the art of scanning electron microscope*, Columbia University Press, New York, 1996, pp. 166–168.

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