

Formation Mechanism of Mg_2SiO_4 Fishbone-like Fractal Nanostructures

Songhai Xie,^{†,‡} Wuzong Zhou,^{*,†} and Yanqiu Zhu[§]

School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK, and School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Received: January 23, 2004; In Final Form: April 15, 2004

Mg_2SiO_4 fishbone-like fractal nanostructures have been investigated using high-resolution transmission electron microscopy. The branches of Mg_2SiO_4 fibers and detailed structures of cobalt nanoparticles at different growth stages have been recorded, and the formation mechanisms of both the fibers and the Co nanoparticles are discussed. It was found that these two components grew concurrently. Co initially formed nanocrystallites with sizes less than 5 nm and these nanocrystallites joined together to form spherical clusters. These clusters continued to grow and recrystallized into larger polygonal single crystals (> 150 nm). The experimental evidence shows that the formation process of Mg_2SiO_4 includes amorphous surface coating, forming polycrystallites in the coating layer and recrystallizing into cylindrical main stems and branches.

I. Introduction

Fractal structures are often found in nature, such as leaves, snow crystals, and coral. This concept originally came from mathematics. However, these fantastic structural profiles have now been investigated in other research fields, such as chemistry, physics, and materials sciences, and have attracted many researchers for years due to their self-similarity and semiorganizing. As a large family of materials, dendrite crystals, representing fractal structures, have been studied extensively for their interesting crystallizing behavior in past decades;^{1–9} for example, $\text{PbS}^{4,5}$ and Sb_2S_3 ⁶ were synthesized by a solvent–thermal method, silver dendrites were made by subtracting Raney Ni as hard template,⁷ and SnO_2 ⁸ and MgO ⁹ were prepared via calcinations at high temperature. Most of the work focused on the novel morphologies, the elemental compositions, and the orientations of crystal growth. However, the mechanisms for the formation of these fractal crystals were hardly investigated apart from some simulated models being proposed on the basis of theoretical considerations.^{1,10–13}

In a previous report,⁹ Cocatalyzed growth of three-dimensional fractal fishbone-like Mg–Si–O crystals was presented and both vapor–liquid–solid (V–L–S) and nucleation–aggregation (N–A) mechanisms were applied in order to interpret the crystal growth with such an elegant structure. The particle forms by one main stem with a Co catalytic particle at the end, and many secondary branches, also having Co particles at the tops, grow randomly from the surface of the Mg–Si–O stem. The secondary branches are almost perpendicular to the main stem. Smaller subsecondary branches then grow on the surface of the secondary branches, and so on (Figure 1). It was proposed that MgO/SiO_2 vapor mixture diffuses and condenses onto the Co particle surface, forming a complex Co–Mg–Si–O

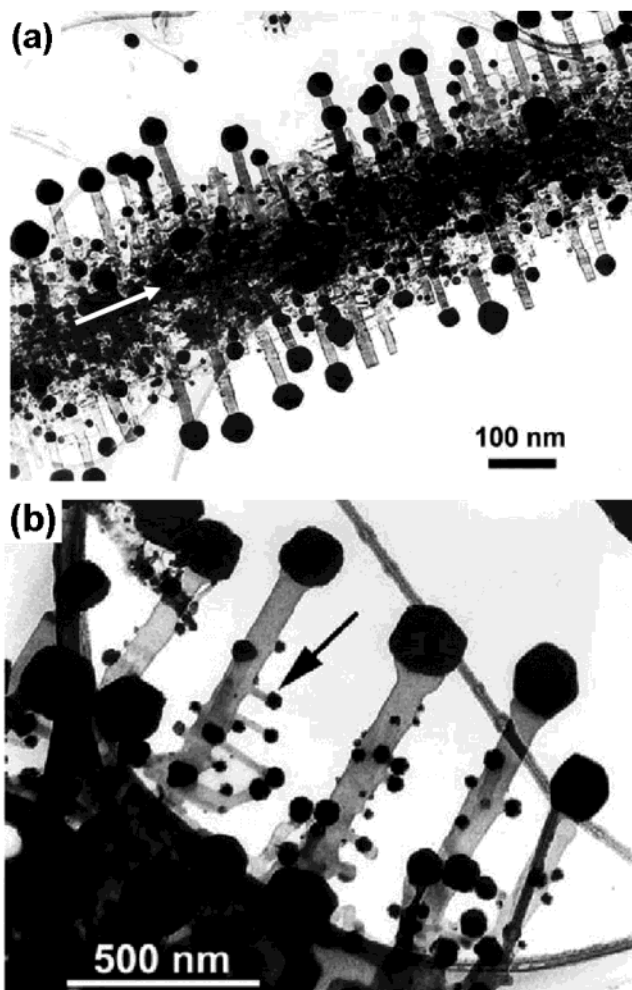


Figure 1. (a) Low-magnification image of a fishbone-like nanoparticle showing the main stem indicated by the arrow and secondary branches with the cocatalytic nanoparticles at the top ends. (b) Higher magnification picture showing lollipop-like secondary branches and mini-lollipop-like subsecondary branches indicated by an arrow.

* To whom correspondence may be addressed. E-mail: wzhou@st-andrews.ac.uk.

[†] University of St. Andrews.

[‡] Permanent address: Department of Chemistry, Fudan University, Shanghai, China.

[§] University of Nottingham.

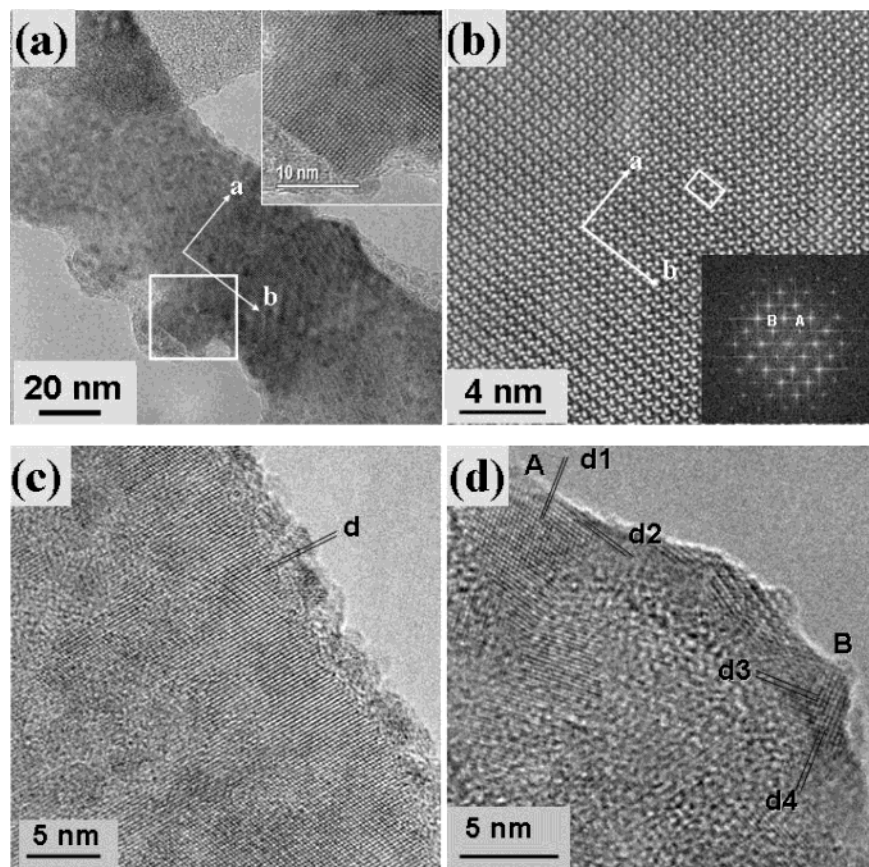


Figure 2. (a) TEM image of a secondary branch of a Mg_2SiO_4 fishbone-like fiber with at least two subsecondary branches. The Co particles have been lost during the specimen preparation. The inset is an enlarged image of the junction area between the secondary branch and one of the subsecondary branches marked by the square. (b) HRTEM image of a small area of the particle in part a. The view direction is the $[001]$ zone axis of Mg_2SiO_4 . The rectangular mark shows a unit cell of Mg_2SiO_4 . The zone axes of A and B are indicated in both parts a and b. (c) HRTEM image of a secondary branch showing many nanoparticles on the surface. $d = 0.27$ nm. (d) An enlarged surface profile image of a secondary branch showing some nanoparticles in the surface amorphous coating layer. Particle A is an image of Co nanoparticle with d spacings of $d_1 = 0.205$ nm and $d_2 = 0.205$ nm viewed down the $[110]$ direction. Particle B is a 2D image of Mg_2SiO_4 with d spacings of $d_3 = 0.25$ nm and $d_4 = 0.29$ nm when viewed down the $[001]$ zone axis.

fluid phase. A Mg/Si oxide crystal starts to grow on the Co surface and the process continues at the interface of the Co particle and the oxide crystal. This is known as the V–L–S mechanism.¹⁴ To understand the stacking fractal structure, it was believed that Co particles randomly deposited on the oxide surface and subbranches grow underneath the Co particles. This follows the principle of the so-called N–A mechanism.¹⁵ Even after the above two mechanisms were applied, the formation of the fractal structure still cannot be fully understood. For example, the Co particles seem to grow with the oxide stems so that the longer the stems, the larger the Co particles, as seen in Figure 1. In a normal catalytic process, the diameter of the nanowires depends on the size of catalytic particles and it does not change after the nanowires form on the surface of the catalyst. It can be easily found that the oxide crystal stems presented in Figure 1 grow three-dimensionally and therefore the diameter of a stem increases with its length and is almost uniform along the stem axis. It is believed that there must be some mysterious steps in the formation of these nanostructures.

It is our principal objective to reinvestigate the detailed structures of these materials by using high-resolution transmission electron microscopy (HRTEM), a powerful technique for revealing local structures of solids including the surface structures at atomic resolution.¹⁶ To study a formation mechanism, we normally need to investigate specimen structures at different stages of the crystal growth. In the present work, this problem becomes much simpler, since the length of an oxide

stem is a function of the growth time and oxide stems with different lengths can be easily found in a single “fishbone”. We were therefore able to image the detailed structures of the Co particles and the Mg/Si oxide stems at different stages of their growth and discovered that the formation mechanism of this material is much more complicated than we previously expected.

II. Experimental Section

The experimental conditions for synthesis of fishbone-like Mg/Si oxide were described in the previous papers.^{9,17} A mixture of Mg/Si containing Al_2O_3 and Co powders was supported on a Al_2O_3 plate and heated at ca. 1600 °C for about 30 min in a chamber filled with CO gas at ca. 200 Torr. The fishbone-like materials were collected at the edge of the apparatus. The specimen for the HRTEM analysis was dispersed in ethanol followed by ultrasonic treatment. One drop of the suspension was deposited on a specimen grid with a holey carbon film. HRTEM and TEM images were recorded using a Gatan CCD camera attached to a JEOL JEM-2011 electron microscope operated at 200 kV. Images were recorded at magnifications of 100 000–800 000 times. Chemical composition of the specimen was examined by energy-dispersive X-ray microanalysis (EDX).

III. Results and Discussion

Point analysis and elemental mapping of EDX show that both the main stem and sub-branches consist of Mg, Si, and O and

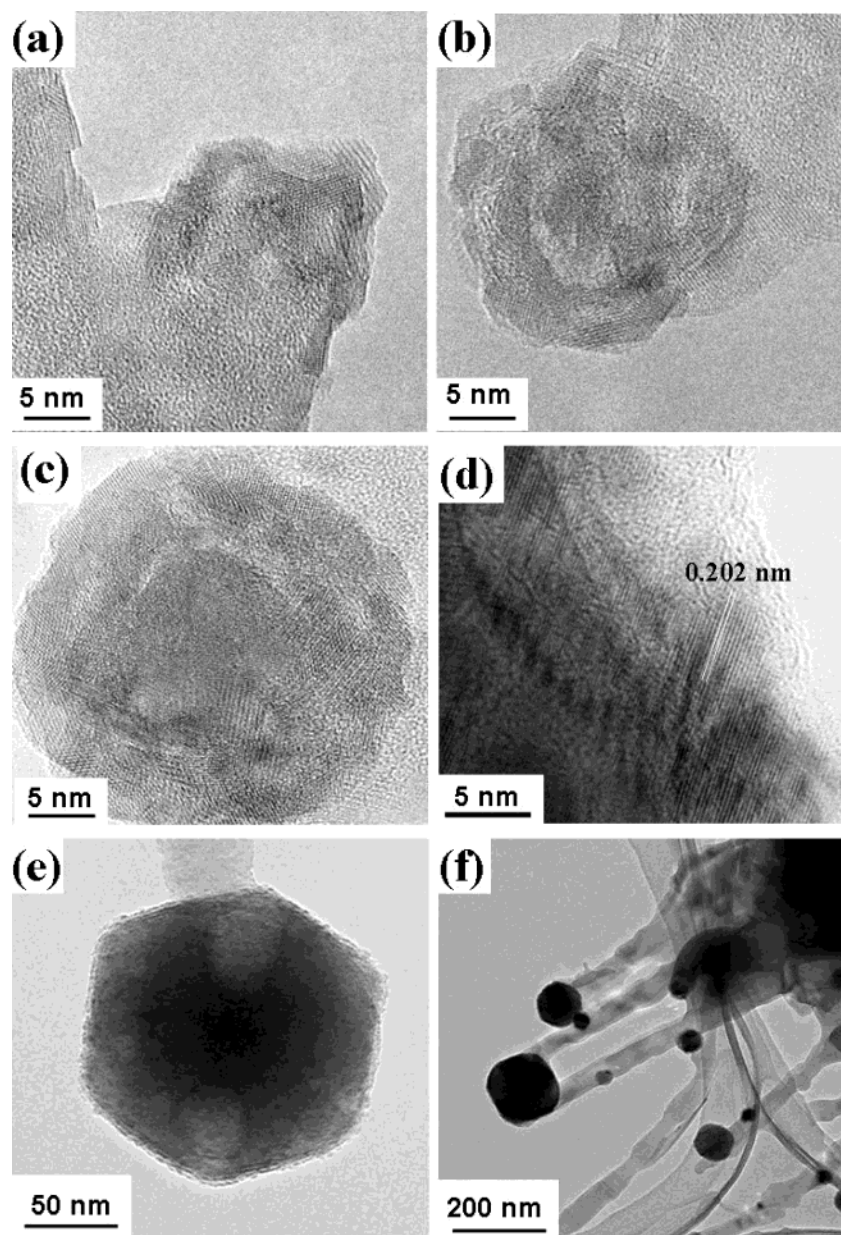


Figure 3. HRTEM images of Co particles at different growth stages. (a) A small Co cluster on the Mg₂SiO₄ surface. (b and c) Spherical clusters of Co nanocrystallites in different diameters. (d) HRTEM image of an edge area of a polygonal Co particle, showing a large domain of a Co single crystal. (e) TEM image of a polygonal particle of Co. (f) A polygonal Co particle resulted from recrystallization of two clusters originally located at the ends of two Mg₂SiO₄ branches.

the particles at the ends of branches are pure Co metal. Although the content of Si varies, the ratio of Mg:Si from most branches is about 2:1, implying a possible crystalline phase of Mg₂SiO₄.

Figure 2a is a low-magnification TEM image of a typical secondary branch of oxide with at least two very short subsecondary branches. The inset of Figure 2a is an enlarged HRTEM image of the junction area marked by a square. It is confirmed that the fiber is a single crystal and the subsecondary branch grows perfectly with the secondary branch. Two principal *d* spacings of 0.51 and 0.59 nm were measured from the image, corresponding to the (020) and (100) planes, respectively, in the orthorhombic unit cell of Mg₂SiO₄ with *a* = 0.59 and *b* = 1.02 nm. This result concurs with the reported unit cell dimensions of the compound, *a* = 0.59817 nm, *b* = 1.01978 nm, and *c* = 0.47553 nm, space group *Pmnb* (62) (PDF 34-189). Figure 2b is a HRTEM image of a part of the fiber shown in Figure 2a, revealing the (040) (*d* = 0.255 nm) and (200) (*d* = 0.297 nm) atomic planes. Consequently, the view direction

of the images in Figure 1a,b is the [001] zone axis. The direction of the crystal growth of the secondary branch shown in Figure 2a is along the [010] zone axis and that of the subsecondary branch is along the [100] direction of Mg₂SiO₄. The angle between these two directions is obviously 90°.

We have noticed that Ding et al. just published a paper about Sn-guided ZnO nanowires. They found that the orientations of the nanowires have a strong relation with the crystal orientations of the catalytic Sn particles.¹⁸ The formation of the 1D nanostructures showed a typical example of the VLS process. However, the observed phenomenon in Cocatalyzed Mg₂SiO₄ nanorods, in the present work, is quite different. We actually examined many branches of the oxide and found that the orientation of the crystals is variable, although the angles in the junctions are almost constant, which can be seen from Figure 1. For example, the *d* spacing along the branch axis in Figure 2c is about 0.27 nm, corresponding to the (031) planes of Mg₂SiO₄. The junction angle seems to be independent to the crystal orientation.

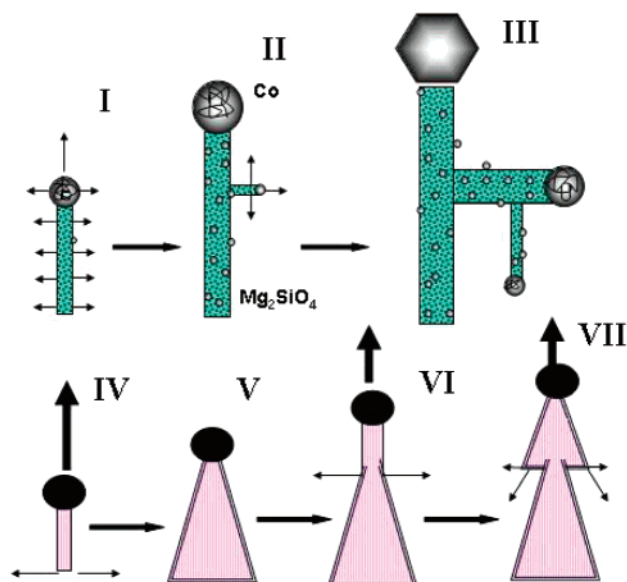


Figure 4. Schematic drawing of crystal growth of Co nanoparticles and Mg_2SiO_4 fishbone-like fibers. I–III show how the typical fractal structure is produced. IV–VII show the possible formation route of a conelike structure.

When we saw the lollipop-like secondary branches during the TEM examination, we found that the diameters of the stems never changed, even after tilting the specimen grid to a large angle, e.g. up to 30° . The stems are therefore cylindrical.

In Figure 2a, we can see many black spots. These spots are actually nanoparticles on the surface of the branch. They become obvious in HRTEM images, as seen in Figure 2c,d. On the surface of almost all the Mg_2SiO_4 branches there is an amorphous coating layer in which many nanoparticles are immersed. This phenomenon is expected in the N–A mechanism.¹⁵ However, the HRTEM surface profile images reveal structural details beyond what the N–A process predicts. Measurement of the d spacings in the images confirms that there are nanoparticles of Co metal as well as Mg and Si oxides. For example, the particle A in Figure 2d shows two d spacings of about 0.205 nm, both fitting to the distances of the (111) planes of face-centered cubic Co. The view direction of the image is then the [110] zone axis. Particle B has larger d spacings of about 0.245 and 0.288 nm. Both values match the d spacings of the (040) and (200) planes of Mg_2SiO_4 , respectively.

It should be noted that the Mg_2SiO_4 phase does not normally form until the temperature reaches ca. 1900°C according to the ternary phase diagram of SiO_2 – Al_2O_3 – MgO ,¹⁹ whereas in the present work the experimental temperature was maintained at 1600°C . We believe that this unusual phenomenon arises for the following reasons. At 1600°C (200 Torr), MgO (mp 2852°C) is far below its respective melting point and only the melting point of SiO_2 (1723°C) is approached. Catalyzed by Co or Fe, SiO_x fibers have been produced under similar conditions.¹³ However, when the oxides exist in a mixture (e.g. $\text{MgO} + \text{SiO}_2$, or $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2$), the melting point drops dramatically to 1545 and 1557°C , respectively. Therefore the presence of variable SiO_2 composition in our system is significant for the fishbone growth. The higher the SiO_2 concentration, the easier the forsterite Mg_2SiO_4 fibers grow. Hence, the temperature (1600°C) is high enough for the V–L–S growth process for the fishbone fibers. Meanwhile, the cobalt catalyst in the surface coating layer will favor Mg_2SiO_4 nanocrystallites to form first within the amorphous coating

layer and then recrystallize with the core Mg_2SiO_4 crystal. It therefore can be understood why the stems continue to grow on the side, forming an almost perfect cylindrical morphology with a smooth surface. This mechanism is different from the conventional one in which no amorphous layer is assumed to be present and individual atoms deposit directly on the surface crystallographic sites. Consequently, favored crystal facets are normally seen on the surface.

The crystal growth at the top of the branches is also catalyzed by the relatively larger Co particles, as seen in Figure 1, and we think the V–L–S mechanism can be used to explain the phenomenon. Most research stopped at this point without further investigation on the detailed structures of the Co particles and how they grow from very small crystallites (about 2 nm in diameter) in the surface layer into large (150 nm or more in diameter) ones. It is partially because lattice images are hardly observed when the diameter of a particle is too large, although it is quite possible to image the atomic structure when the particle size is on a nanometer scale.²⁰ In the present work, we tried to investigate detailed structures of the Co particles with different sizes corresponding to different growth stages.

Figure 3a is a small preliminary cluster of Co nanocrystallites on the surface of an Mg_2SiO_4 stem. The sizes of the nanocrystallites are in a range from 2 to 5 nm. They aggregated within the surface amorphous layer as we can expect from the nucleation–aggregation mechanism. In Figure 3b,c, we can see how the clusters grew when the number of Co nanocrystallites increased. The clusters initially had an irregular shape and then became spherical ones gradually. At these stages, the clusters of Co were less condensed and looked like porous material due to the space between the nanocrystallites. The nanocrystallites aggregated in the cluster, eventually recrystallize into larger crystals, as seen in Figure 3d, where some crystallites grow together with the same orientation. In this case, the central area of the particle became highly condensed and the specimen was too thick for HRTEM imaging. However, structural images can be observed at the edges. Finally, some type of polygonal morphologies appeared, as shown in Figure 3e,f. The final form of Co particles was a single crystal. However, many structural defects were still commonly observed. The growth of Mg_2SiO_4 stems started from the very beginning instead of after the polygonal Co particles formed. Figure 3f shows that two Mg_2SiO_4 branches grow parallel to each other. The Co clusters at the ends of these two branches could have been very close and touched each other when their sizes were large enough so that they accidentally recrystallized into one single crystal. This phenomenon has been often observed when Co catalyzes the SiO_x nanoflower growth.¹⁷ Consequently, a dual-catalytic mechanism seems to be a reasonable explanation of this process; i.e., Co catalyzes the Mg_2SiO_4 growth both at the ends of the branches and on the side surfaces, and the Mg_2SiO_4 crystals catalyze the growth of Co clusters simultaneously.

According to the above discussion, the formation of a cylindrical Mg_2SiO_4 branch depends on their simultaneous three-dimensional growth, thus the size of the Co particle must carry on growing to match and catalyze such concurrent growth. The top route of Figure 4 is a schematic drawing to show this process. Panel I shows a lollipop-like branch of Mg_2SiO_4 with a polycrystalline Co cluster on the top. The Mg_2SiO_4 branch grows three-dimensionally, indicated by the arrows, as more nanocrystallites join in a surface amorphous coating layer and then recrystallize with the core crystal. The Co nanocrystallites in the surface coating layer aggregate into new clusters, and

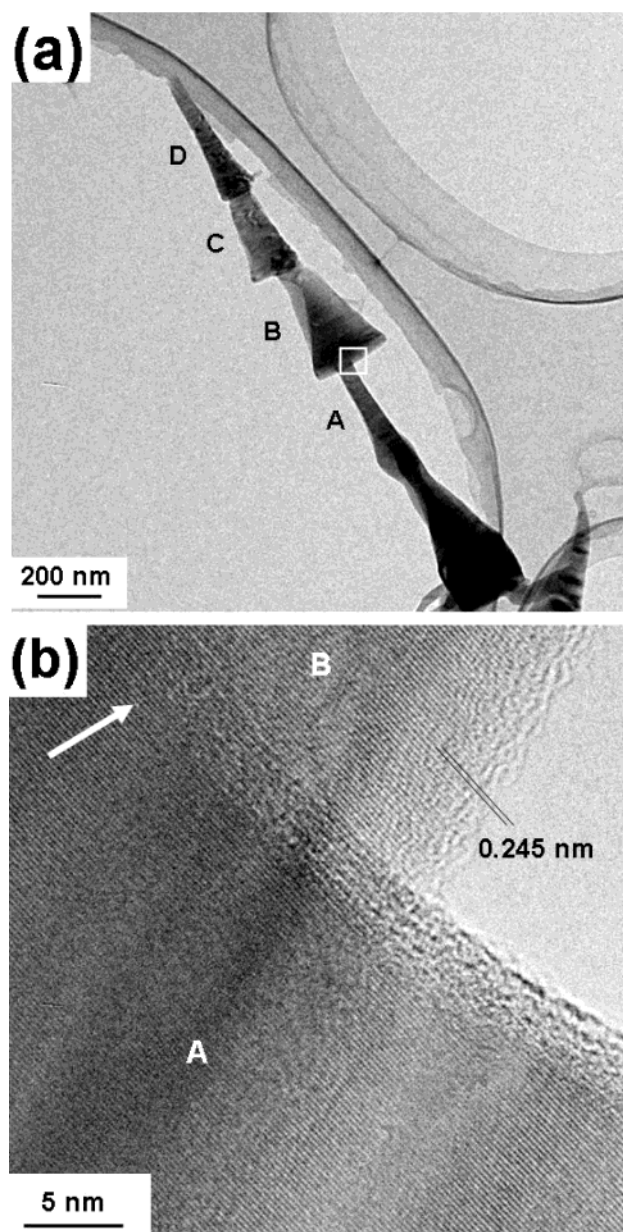


Figure 5. (a) TEM image of a stem of Mg₂SiO₄ consisting of some conelike particles. (b) HRTEM image of a junction area between the cones A and B marked in part a showing the same crystal orientation. The arrow shows the crystal connection between cones A and B.

some secondary branches grow underneath the Co clusters presented in panel II. The spherically shaped polycrystalline Co clusters also grow when more nanocrystallites form on their surface. The Co clusters eventually recrystallize into the polygonal single crystals shown in panel III.

If the Co growth stops while the growth of Mg₂SiO₄ on the side surface carries on, or the growth rate of the Co cluster is much slower than that of the Mg₂SiO₄ stem, the diameter of the Mg₂SiO₄ stem near the Co particle must be smaller than that of the other end. The final morphology would be cone-like. This rare shape was indeed occasionally observed. For example, shown in Figure 5a, there are four or more cones lining up into a nanorod. Figure 5b is a HRTEM image of a junction area between the cones A and B. It is found that each cone is a single crystal with a thin amorphous coating layer. The *d* spacing observed from the image is about 0.245 nm, corresponding to the (040) planes of Mg₂SiO₄. Furthermore, the cones have exactly the same crystal orientations and per-

fectly intergrow with each other, as indicated in Figure 5b. A schematic drawing of possible formation mechanism of the cone structure is shown by the bottom route in Figure 4. Using the mechanism proposed above, we may explain the formation of the cone structure. However, we are unable to understand why the first cone's growth stops and the growth of the second cone starts and so on. We noticed that the surface coating on the cone crystals is free of nanocrystallites (Figure 5b). This is probably related to the depression of the crystal growth.

IV. Conclusion

Cocatalyzed growth of fishbone-like fractal Mg₂SiO₄ nanostructures has been studied. According to the HRTEM images and EDX microanalysis, the formation mechanism of this material is far more complicated than what we normally expected. We have demonstrated that Co and Mg₂SiO₄ crystals grow simultaneously during the reaction, and a dual-catalytic process has been proposed. Second, experimental evidence has shown that the polygonal Co particles were the final form. We found that Co formed nanocrystallites of 2–5 nm in diameter in the surface coating layer of the Mg₂SiO₄ crystalline stems and then aggregated into large clusters. These clusters further grew and recrystallized into polygonal single crystals. Instead of the single crystals, it was the polycrystalline clusters that played the most important role in Mg₂SiO₄ growth. Third, the growth of Mg₂SiO₄ stems was three-dimensional. Mg, Si, and O atoms deposited on the surface of the stems to form an amorphous coating layer preliminary. Some Mg₂SiO₄ nanocrystallites 5 nm or less in diameter developed in this coating layer, probably catalyzed by the individual Co nanoparticles that were also present in this layer. The Mg₂SiO₄ nanocrystallites then recrystallized into the core crystal. Using this mechanism, we can explain why the shape of the Mg₂SiO₄ stems is almost perfectly cylindrical and the angles between the main stem and the secondary branches and between secondary branches and subsecondary branches are independent of the crystal orientation.

Acknowledgment. We thank SHEFC and EPSRC for financial support. S.X. gratefully acknowledges Fudan University, Shanghai, for the visiting scholarship to St. Andrews University.

References and Notes

- (1) Hoyt, J. J.; Asta, M.; Karma, A. *Mater. Sci. Eng. R—Rep.* **2003**, *41*, 121.
- (2) Alkemper, J.; Mendoza, R.; Voorhees, P. W. *Adv. Eng. Mater.* **2002**, *4*, 694.
- (3) Tian, Z. R. R.; Liu, J.; Voigt, J. A.; Xu, H. F.; Mcdermot, M. J. *Nano Lett.* **2003**, *3*, 89.
- (4) Wang, D.; Yu, D. B.; Shao, M. W.; Liu, X. M.; Yu, W. C.; Qian, Y. T. *J. Cryst. Growth* **2003**, *257*, 384.
- (5) Kuang, D.; Xu, A.; Fang, Y.; Liu, H.; Frommen, C.; Fenske, D. *Adv. Mater.* **2003**, *15*, 1747.
- (6) Mo, M. S.; Zhu, Z. Y.; Yang, X. G.; Liu, X. Y.; Zhang, S. Y.; Gao, J.; Qian, Y. T. *J. Cryst. Growth* **2003**, *256*, 377.
- (7) Xiao, J. P.; Xie, Y.; Tang, R.; Chen, M.; Tian, X. B. *Adv. Mater.* **2001**, *13*, 1887.
- (8) Hu, J. Q.; Bando, Y.; Golberg, D. *Chem. Phys. Lett.* **2003**, *372*, 758.
- (9) Zhu, Y. Q.; Hsu, W. K.; Zhou, W. Z.; Terrones, M.; Kroto, H. W.; Walton, D. R. M. *Chem. Phys. Lett.* **2001**, *347*, 337.
- (10) Wang, W.; Kermanpur, A.; Lee, P. D.; Mclean, M. J. *Mater. Sci.* **2003**, *38*, 4385.

- (11) Levin, P. *Phys. Lett. A* **2003**, 310, 383.
- (12) Granasy, L.; Borzsonyi, T.; Pusztai, T. *Phys. Rev. Lett.* **2002**, 88, art. no. 206105.
- (13) Suzuki, T.; Ode, M.; Kim, S. G.; Kim, W. T. *J. Cryst. Growth* **2002**, 237, 125.
- (14) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, 4, 89.
- (15) Zhang, J. Z.; Ye, X. Y.; Yang, X. J.; Liu, D. *Phys. Rev. B* **1997**, 55, 5796.
- (16) Zhou, W.; Thomas, J. M. *Curr. Opin. Solid State Mater. Sci.* **2001**, 5, 75.
- (17) Zhu, Y. Q.; Hsu, W. K.; Terrones, M.; Geobert, N.; Terrones, H.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Mater. Chem.* **1998**, 8, 1859.
- (18) Ding, Y.; Gao, P. X.; Wang, Z. L. *J. Am. Chem. Soc.* **2004**, 126, 2066.
- (19) Linda, R. P.; George, H. B. *J. Noncryst. Solids* **1997**, 219, 219.
- (20) Ley, S. V.; Mitchell, C.; Pears, D.; Ramarao, C.; Yu, J.; Zhou, W. *Org. Lett.* **2003**, 5, 4665.