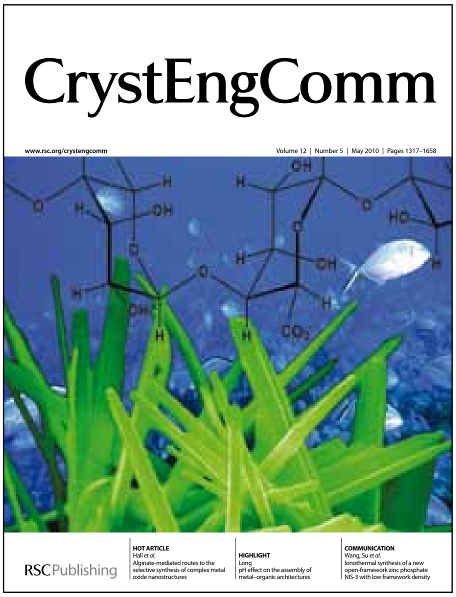
CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSC Publishing

www.rsc.org/crystengcomm
Registered Charity Number 207890

A Compromise between Competing Forces Dominating the Diversity of Aragonite Structures

Han Wang[1,2], *Yongsheng Han*[1,*]

1 EMMS Group, State Key Laboratory of Multiphase Complex Systems,
Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China,
2 University of Chinese Academy of Sciences, Beijing, 100490, China
E-mail: (yshan@home.ipe.ac.cn)

Keywords: (nanoparticles, aragonite, shape diversity, shape control)

Abstract

Material scientists have strong interests in disclosing the reason causing the diversity of material structure. Here, we show a different story in disclosing the mechanism dominating material structures. When we synthesize calcium carbonate particles at increased temperatures, we observe that the structures of particles change with temperature. At a relatively low temperature (60℃), the dumbbell shaped particles are largely formed while the straight particles are dominantly formed at a relatively high temperature (90℃). By simulation, we find that the crystallite of aragonite is polarized after the adsorption of water molecules on its surface. The polarization is anisotropy, which make the attachment of crystallites have different stability along different attaching directions. At an increased temperature, the attachment is easily destructed by Brownian motion which is dependent on temperature. Therefore, the adsorbing force provided by polarization competes with the destructive force induced by the Brownian motion. The compromise between these two competing forces dominates the stable structure of calcium carbonate particles. Hence, the compromise in competition between attractive force and destructive force leads to the diversity of aragonite structures, which promises a new direction to discover the diversity of materials structure.

1. Introduction

Chemists and materialists have achieved great progresses in synthesizing materials with amazing structures.[1-5] But the discovery on the formation mechanism of these structures are far behind, which becomes a bottleneck to scale up the production of these structures.[6] Fortunately, more and more attentions focus on the black box of material preparation with the aim to disclose the rules or principles governing the structure of materials.[7-9] In the past century, the classical crystallization mechanism characterized as atom-by-atom growth is successful in explaining the growth habit of well-faceted single crystals.[10, 11] However, increasing evidences about the complex structure of crystals from nature and laboratories are challenging this classical textbook mechanism.[12,13] For example, sea urchin spine behaves like a single crystal in polarization microscopy or scattering experiments, but its morphology is highly curved and has an overall sponge-like inner structure, showing no crystal faces at all.[14] Materials with such structure are abundant in nature and frequently synthesized in laboratories, which triggers intensive studies on crystallization. In the past decade a non-classical crystallization pathway based on oriented attachment of particles has been developed. This growth process was first highlighted by Banfield's group,[15-17] and further developed by Cölfen's group.[18-21]

The non-classical crystallization often involves the nucleation of primary particles followed by their oriented attachment towards "mesocrystals". These mesocrystals often exhibit substantial preferred orientation.[22,23] In the process of primary particle assembly, directional physical fields, such as electric, magnetic, or dipole fields, are the most probable forces accounting for the ordering alignment of particles.[14] Oriented attachment induced by directional physical fields can successfully explain the epitaxial growth along one direction in which there exists the strongest attraction force between primary particles. However, for a system with more complex structures, oriented attachment is not sufficient to interpret its complexity. For example, in the preparation of Sb_2S_3 nanoparticles, oriented attachment leads to the formation of nanorods to bundles.[24] However, with the elongation of the hydrothermal time, the morphology of the bundles switches to close-packed spheres. Therefore, in addition to the oriented attachment, other forces may exist and or even become dominant in the later stage of hydrothermal treatment. These forces compete with directional force, leading to the disassembly of oriented attachment and forming spherical balls. In our previous studies, it is discovered that the compromise in competition between dominant factors plays important roles in shaping structures, which has been verified in different systems.[25,26] And the snow-shaped vaterite particles have been firstly synthesized by the compromise between diffusion and reaction. [27]

In this paper we show another story in disclosing the roles of compromise between dominant factors in shaping structures of materials. The rod-like particles are dominantly formed when calcium carbonate particles were synthesized at an increased temperature. When the temperature was carefully tunned, particles switch from dumbbell shape to straight rods with the increase of temperature. To the best of our knowledge, this is the first observation on the switch of such structures. In this paper, we are going to answer two questions. First, why the rod like particles are predominantly formed at an increased temperature? Second, why the shapes of rod particles changes with temperature?

2. Results and Discussions

The samples synthesized at different temperatures (60℃, 70℃, 80℃, 90℃) were characterized by scanning electron microscopy, as shown in Figure 1. Figure 1a to 1d show the low magnification images of the products synthesized at 60℃ to 90℃, revealing high yields of the particles with uniform morphology. Magnifications on the particles as shown in Figure 1e to 1h show that the particles synthesized at different temperature have remarkably different morphology. The particles synthesized at low temperature (60℃) show dumbbell shape with a rod-like handle and two radial ends (Figure 1e). While at a relatively higher temperature (70℃), the spiking branches at two ends are reduced and the handle become longer. As the temperature is increased to 80℃, the radial ends disappear while the splitting ends show up. As the temperature is increased to 90℃, the splitting ends are reduced and straight rods with a few Y-shaped ends form. Phase identification on the obtained products was carried out by powder X-ray diffractometry (XRD), as shown in Figure 2. In accordance with the JCPDS file of No. 05-0453, these diffraction peaks can be indexed to orthorhombic aragonite with lattice parameters of a_0 = 4.959 Å, b_0 = 7.968 Å, c_0 = 5.741 Å), suggesting that the products are mostly aragonite.

In order to get detailed information on the aragonite structures, the samples were characterized by high resolution SEM and TEM. Figure 3a shows a high magnification SEM image of the aragonite particle synthesized at 60℃. Careful observation on the handle part of the particle shows that the handle is built up by the assembly of nanoscale crystallites. These crystallites are not only assembled end-to-end and side-to-side, but also fused together, which have the typical mesocrystal features proposed by Cölfen etc.[18,20] At the ends of the particle, the crystallites show massively radial aggregation, where we can observe end-to-side attachment. Figure 3b shows a SEM image of the particles synthesized at 90℃. Compared to the dumbbell-like particles in Figure 3a, Figure 3b exhibits stick-like structure with Y-shaped ends instead of radial ends. The TEM image in Figure 3c confirms that the aragonite particles are built up by small crystallites. Figure 3d and its inset are representative HRTEM image and SAED pattern taken from the crystallites shown in Figure 3c. In Figure 3d, possible attachment schemes (white-line box) by four primary crystallites are outlined, which gives us direct evidence on the crystallographic orientation of the crystallites. Red marks in Figure 3d show slight stack fault and angular misorientation between the adjacent assemble crystallites. The fringe spacing distance perpendicular and parallel to the long axis of the rod are 5.75 Å and 7.97 Å which correspond to the distances of (001) and (010) planes of the aragonite, respectively, indicating that the c-to-c attachment and b-to-b attachment are present in the assembly. Therefore, we could conclude that the aragonite particle is built up by small crystallites following certain crystallographic orientation. Now we are curious about what is the driving force for the orderly assembly of crystallites and why the structures of particles changes with temperature. Above questions will be discussed in the following studies

Due to the highly ordered alignment of crystallites, we speculate that certain intrinsic interactions between the crystallites should exist. Previous studies suggest that there may exist anisotropic dipole moment in the crystallites of aragonite as a result of the noncentrosymmetric arrangement of calcium ions and carbonate ions.[28,29] But this suggestion is based on groundless speculations without direct evidence. On the other hand, it has been proved that the presence of surface species may facilitate the orientation of contacting particles[30] and the solvent molecules largely influence the interactions among building blocks.[31, 32] Therefore, we speculate that the adsorption of water molecules on the surface of aragonite crystallites may be responsible for the oriented attachment of crystallites. Therefore, we conduct molecular simulation to testify this speculation as follows.

A 2×1×2 supercell of orthorhombic aragonite was chosen as the study crystallite. The interactions between water molecules and the crystallite are simulated using Adsorption Locator Module, by which the most probable adsorption configuration is identified. After energy calculation on the obtained crystallite via Dmol^3 module, anistropic dipole moment along three axis of the crystallite is identified, which is believed to be induced by the adsorption of water molecules. The bar graph in Figure 4 shows the calculated value of the dipole moment of the crystallite along each axis.

The 3D atomistic structures above each bar in Figure 4 show the representative adsorption configuration on the facets. The calculating results indicate that the study cell becomes polar after the adsorption of water molecules and the dipole moment along [001] direction is the strongest. Because the dipole force along the [001] direction is the strongest, the attachment of the crystallites prefer to occur between the (001) faces, making the preferential growth of aragonite particles and forming rod-like particles, as illustrated in Figure 5. Therefore, the aragonite particles dominantly show rod-like shape as a result of preferential attachment. To the best of our knowledge, this is the first simulation work supporting the existence of anisotropic dipole moment of the aragonite crystallites. From now on, we want to discover why the aragonite structure changes with temperature.

Based on the dipole moment along each axis in Figure 4, we can conclude that the c to c attachment is most stable while a to a and b to b attachment is less stable. The attachment between c to a/b is in the middle value of stability. The c to c attachment corresponds to end to end model while a to a and b to b correspond to side to side model. Others correspond to end to side model. The end to end attachment leads to the growth of particles along c axis while the side to side attachment results in the thickening of particles. The end to side attachment leads to a radial growth of particles. Since the attachment of crystallites is performed in a solution at increased temperatures, the Brownian motion can not be neglected. The “Brownian movement” was named after Robert Brown who first observed uninterrupted and irregular “swarming” motion of pollen of different plants in water.[33] Einstein later proved that the movements of the particles suspended in liquids are a result of thermal molecular motion of the solvent molecules, which are supported by the molecular theory of heat.[34] So Brownian motion is highly temperature-dependent, and it becomes more vigorous with increasing temperature. Brownian motion of crystallites was first proved experimentally[35] and theoretically[36,37] to occur over a single crystal surface. Kyuichi simulated the dipole-dipole interaction of two crystallites, indicating that the Brownian motion is an important factor determining the arrangement of the crystallites.[38] In all cases, the mobility of crystallites in water increases exponentially with the increase of temperature but decreases exponentially with particle size.[22] Thus, we have reason to believe that the crystallites experience vigorous Brownian motion in the formation of mesocrystals. Since the Brownian motion is irregular, it tends to break the oriented arrangement of the crystallites. At low temperature (60-70 ^{o}C), Brownian motion is relatively mild, thus attachment with weaker attraction force, such as side to side attachment, can be broken up. So the products formed at 60-70 ^{o}C have short handle. But the attachments of end to side are dominantly present, leading to the radial growth at the ends of particles. As temperature increases to 80 ^{o}C, the breaking force of Brownian motion becomes stronger. A portion of end-to-side attachments are broken up, leading to the reduction of radial ends. As temperature increases to 90 ^{o}C, most attachments of end-to-side become unstable or not present, resulting in a further reduction of radial ends. At such a high temperature (90 ^{o}C), only the strongest attachment of end-to-end is dominantly present, leading to the formation of straight rods.

Therefore, the change of aragonite structure with temperature is dominated by a competition between two mechanisms, namely assembly driven by dipole force and disassembly driven by Brownian motion. As schematically presented in Figure 6, at a relatively low temperature, the attachment of crystallites is dominated, leading to a three-dimensional growth of particles. While at a relatively high temperature, the Brownian motion breaks the weak attachments, resulting in the formation of simple and finally one-dimension structure. The competition of these two forces exists in all the experiments carried out at different temperatures. Beside the competition, these two forces also rely on each other to realize the diversity of product structures. Without the anisotropic attractive force, the randomly packed particles are probably dominated. Without the destructive forces, all the attachments are possible, which makes the growth of particles losing diversity. Therefore, the competition between these two forces leads to the diverse growth of the particles. Their mutual interaction dominates the diversity of structures. We call this mutual interaction as a compromise effect which is an integrated result of competition and coordination of the dominant factors. We believe that the compromise between competing factors is one of the dominant mechanism (if not the unique), resulting in the diversity and complexity of material structures.

3. Conclusion

A change of aragonite structure with temperature was observed in this paper. The particles formed at a relatively low temperature have dumbbell shape with radial ends while the particles formed at a relatively high temperature have stick shape with few splitting at the ends. To find the reasons causing this change, we conducted molecular simulation on an aragonite crystal cell. The results indicated that the aragonite cell is polarized after the adsorption of water molecules on its surface. The magnitude of polarization is different along each axis. Along the c axis, the polarization is most intensive, which makes the preferential attachment of crystallites in this direction, forming rod-like particles. At the same time, the (001) facet could attach on the (100) and (010) facets, making the radial growth of particles. Nevertheless, the radical attachments are not stable and could be destructed by Brownian motion at a high temperature. So the radial growth is largely suppressed at a high temperature. Therefore, the growth direction of aragonite is dependent on temperature. The structure of aragonite is governed by the compromise in competition between attractive force and destructive force, which change with temperature. The compromise effect is an integrated result, which should be a general rule dominating the diversity and complexity of material structures. We warmly expect that this study gives a new clue to think the diversity of material structure and will be helpful to disclose the formation mechanism of other hierarchical structures.

4. Experimental Details

Materials

$CaCl_2$ (AR grade) and Na_2CO_3 (AR grade) were purchased from Sigma (Beijing, China) and used as received. Aqueous solutions of the reactants were made using Milli-Q high pure water with a resistivity higher than 18 mΩ.

Synthesis of Calcium Carbonate Precipitates

In a typical synthetic process, 0.1mol/L $CaCl_2$ ($NaCO_3$) solution was freshly prepared by dissolving $CaCl_2$ (Na_2CO_3) in pure water. The two solutions were thermostated in a water bath at a given temperature for 20 min. Then the two solutions were instantly mixed together in a 500 ml beaker under vigorous magnetic stirring to form white precipitate. Five minutes later after the mixing, the white precipitate was collected and dried at atmosphere temperature for further characterizations.

Characterizations on Calcium Carbonate Precipitates

The morphologies of samples were characterized on a Hitachi S-4700 scanning electron microscope (SEM) fitted with a field emission source at an accelerating voltage of 20 kV, as well as on a JEM-2100 transmission electron microscope (TEM) at an accelerating voltage of 200kV. The XRD patterns of Samples were recorded on a Siemens D-5000 diffractometer using CuKα (λ=1.5406Å) radiation. The 0.02° step and the 2θ range from 5° to 90° were selected to perform the measurement.

Simulation on the Dipole Moment of Aragonite Crystallites

Computer simulation was conducted on a 2x1x2 aragonite crystal cell with a size of approximate 1 nm along each axis to discover its polarization after the adsorption of water molecules. Three modules in Materials Studio, namely Adsorption Locator, Forcite, and Dmol^3, were used in this study. Adsorption Locator and Forcite are molecule dynamics based modules, whereas Dmol^3 is based on quantum mechanical density-functional theory (DFT). In this computational work, water molecule and aragonite crystal were constructed and their energy was optimized using Forcite classical simulation engine, by which the geometry optimization process was carried out using an iterative process until the total energy of a structure was minimized. Next, in performing Adsorption Locator simulation, adsorbate (water molecules) were randomly distributed within a bounding box enclosing the substrate (aragonite crystallite defined above) at first (Figure 7a). Then, the most probable adsorption configuration (Figure 7b) was identified by carrying out Monte Carlo simulation on the configurational space of adsorbate within the bounding box, as shown in Figure 7. At last, the dipole moment of substrate bound with adsorbate was calculated using Dmol^3 module. In the calculation of the dipole moment, all factors (electronic distribution and nuclear coordinates) that may induce polarity of the crystallite were considered.

Acknowledgements

This study was supported by Hundreds Talent Program from the Chinese Academy of Sciences and the project from the State Key Laboratory of Multiphase Complex Systems (MPCS-2011-C-01). The finance from National Science and Technology Support Program (2012BAA03B03) and Development and Application of Isothermal Differential Micro-fluidized Bed Analyzer for Fluid-solid Reaction were appreciated.

References

1. Y. Sun, X. Hu, W. Luo and Y. Huang, *ACS nano*, 2011, **5**, 7100.
2. J. Su, X. Wu, C. Yang, J. Lee, J. Kim and Y. Guo, *J. Phys. Chem. C*, 2012, **116**, 5019.
3. A. Cao, J. Hu, H. Liang and L. Wan, *Angew. Chem. Int. Ed.*, 2005, **44**, 4391.
4. A. Cao, J. Hu, H. Liang, W. Song, L. Wan, X. He, X. Gao and S. Xia, *J. Phys. Chem. B*, 2006, **110**, 15858.
5. Y. Wang, S. Xie, J. Liu, J. Park, C. Huang and Y. Xia, *Nano Lett.*, 2013, **13**, 2276.
6. I. Y. Goon, L. M. Lai, M. Lim, P. Munroe, J. J. Gooding and R. Amal, *Chem. Mater.*, 2009, **21**, 673.

7. K. K. Ostrikov, I. Levchenko, U. Cvelbar, M. Sunkara and M. Mozetic, *Nanoscale*, 2010, **2**, 2012.
8. J. Yang, J. Zeng, S. Yu, L. Yang, G. Zhou and Y. Qian, *Chem. Mater.*, 2000, **12**, 3259.
9. T. Wang, M. Antonietti and H. Cölfen, *Chem. Eur. J.*, 2006, **12**, 5722.
10. J. W. Mullin, *Crystallization*, Butterworth Heinemann, Oxford, UK, 4th edn., 2001, ch. 6, pp. 216-284.
11. A. L. Washington, M. E. Foley, S. Cheong, L. Quffa, C. J. Breshike, J. Watt, R. D. Tilley and G. F. Strouse, *J. Am. Chem. Soc.*, 2012, **134**, 17046.
12. R. Song, H. Cȯlfen, A. Xu, J. Hartmann and M. Antonietti, *ACS nano*, 2009, **3**, 1966.
13. D. Gebauer, A. Völkel and H. Cölfen, *Science*, 2008, **322**, 1819.
14. H. Cöelfen and M. Antonietti, *Mesocrystals and Nonclassical Crystallization*, John Wiley & Sons Ltd., West Sussex, England, 2008, ch. 3, pp.51-69.
15. R. L. Penn and J. F. Banfield, *Am. Mineral.*, 1998, **83**, 1077.
16. R. L. Penn and J. F. Banfield, *Geochim. Cosmochim. Acta*, 1999, **63**, 1549.
17. R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969.

18. H. Cölfen and M. Antonietti, *Angew. Chem. Int. Ed.*, 2005, **44**, 5576.
19. H. Cölfen and S. Mann, *Angew. Chem. Int. Ed.*, 2003, **42**, 2350.
20. M. Niederberger and H. Cölfen, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3271.
21. K. Lee, W. Wagermaier, A. Masic, K. P. Kommareddy, M. Bennet, I. Manjubala, S. Lee, S. B. Park, H. Cölfen and P. Fratzl, *Nat. Commun.*, 2012, **3**, 1.
22. P. Shen, Y. Fahn and A. Su, *Nano Lett.*, 2001, **1**, 299.
23. M. Ocana, M. Morales and C. Serna, *J. Colloid Interface Sci.*, 1999, **212**, 317.
24. Q. Lu, H. Zeng, Z. Wang, X. Cao and L. Zhang, *Nanotechnology*, 2006, **17**, 2098.
25. J. Li, J. Zhang, W. Ge and X. Liu, *Chem. Eng. Sci.*, 2004, **59**, 1687.
26. G. Ma and J. Li, *Chem. Eng. Sci.*, 2004, **59**, 1711.
27. H. Wang, Y. S. Han and J. H. Li, *Cryst. Growth Des.*, 2013, **13**, 1820.
28. G. T. Zhou, Q. Z. Yao, J. Ni and G. Jin, *Am. Mineral.*, 2009, **94**, 293.
29. P. Tasker, *Journal of Physics C: Solid State Physics*, 1979, **12**, 4977.
30. F. Huang, H. Zhang and J. F. Banfield, *Nano Lett.*, 2003, **3**, 373.

31. N. H. de Leeuw and S. C. Parker, *J. Phys. Chem. B*, 1998, **102**, 2914.

32. P. Raiteri and J. D. Gale, *J. Am. Chem. Soc*, 2010, **132**, 17623.

33. R. Brown, *The Philosophical Magazine, or Annals of Chemistry, Mathematics, Astronomy, Natural History and General Science*, 1828, **4**, 161.

34. A. Einstein, *Annalen der Physik (Leipzig)*, 1905, **17**, 549.

35. A. Masson, J. Métois and R. Kern, *Surf. Sci.*, 1971, **27**, 463.

36. J. Métois, M. Gauch, A. Masson and R. Kern, *Surf. Sci.*, 1972, **30**, 43.

37. R. Kern, A. Masson and J. Métois, *Surf. Sci.*, 1971, **27**, 483.

38. K. Yasui and K. Kato, *J. Phys. Chem. C*, 2011, **116**, 319.

Figure 1. Morphology of aragonite particles synthesized at different temperatures (a and e: 60℃; b and f: 70℃; c and g: 80℃; d and h: 90℃). e-h is the magnified images of a-d, respectively.

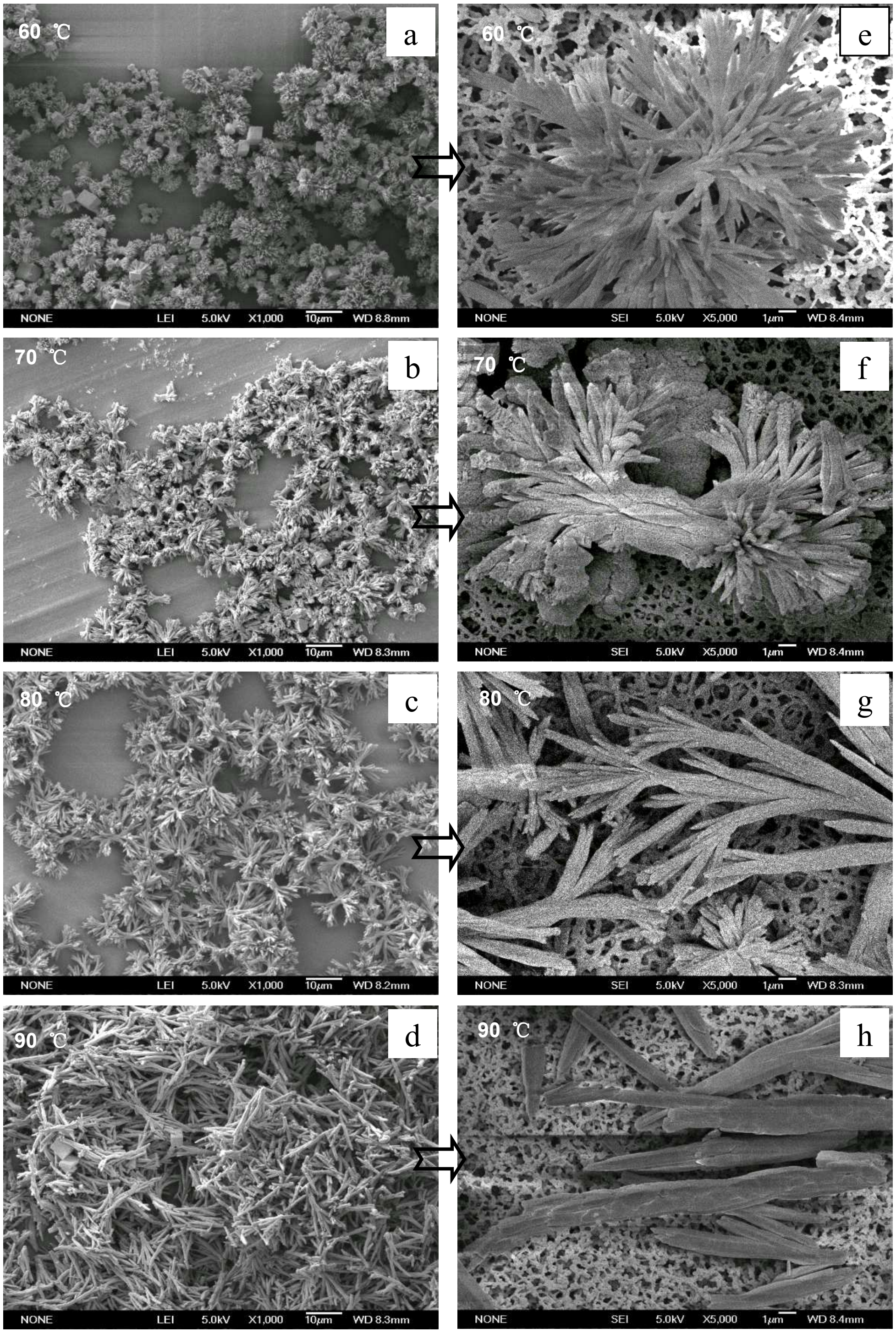


Figure 2. XRD patterns of samples synthesized at different temperatures. It indicates that the aragonite is the main composition of the samples synthesized at high temperature.

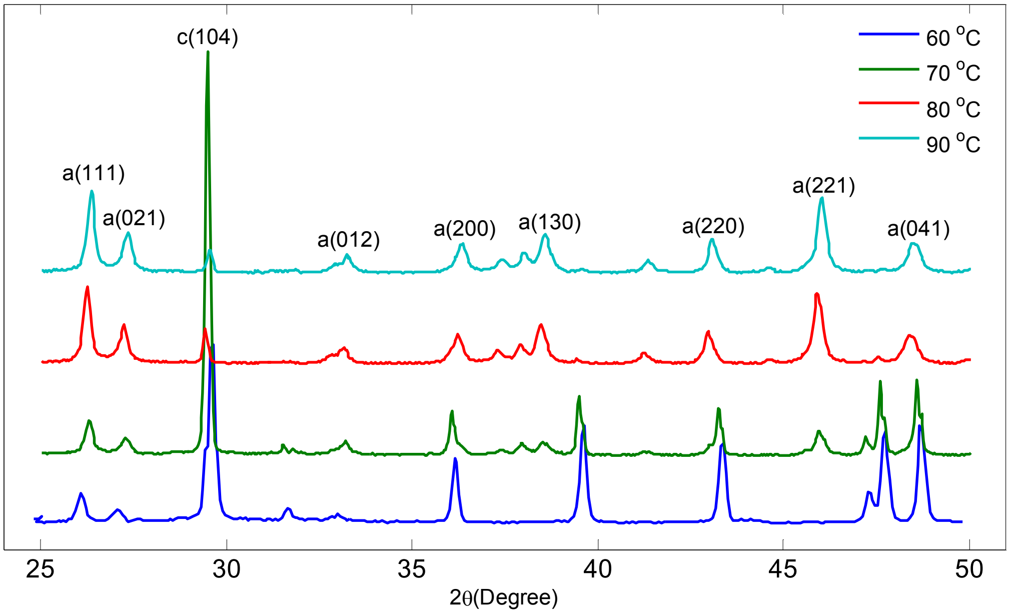


Figure 3. High resolution characterizations on aragonite particles by SEM and TEM.

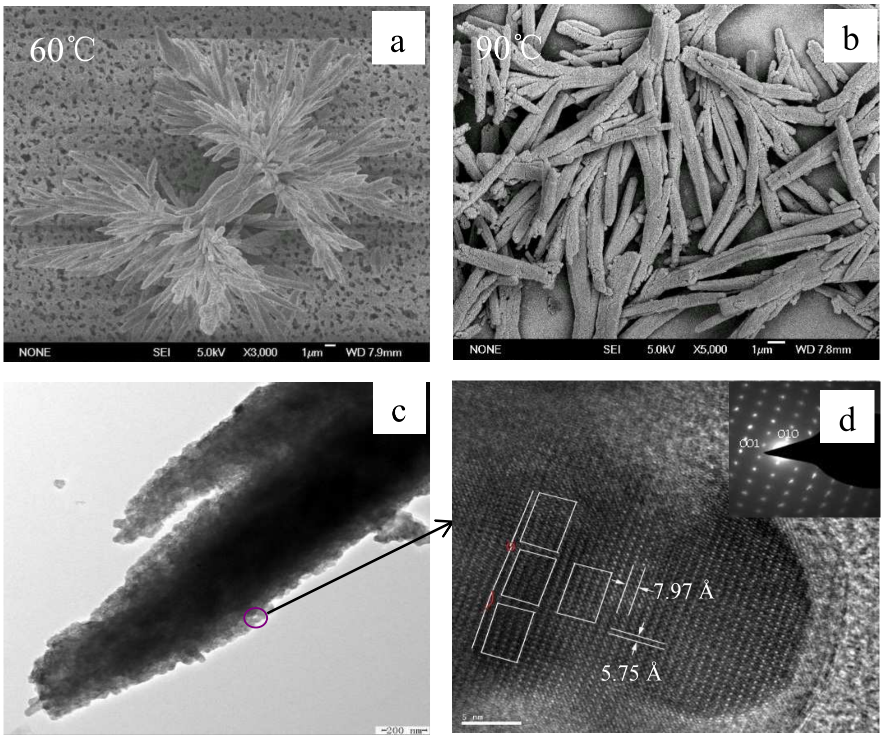


Figure 4. Simulating dipole moment of an aragonite crystal cell along each axis. The insets illustrate the adsorption of water molecules on the surface of the crystal cell.

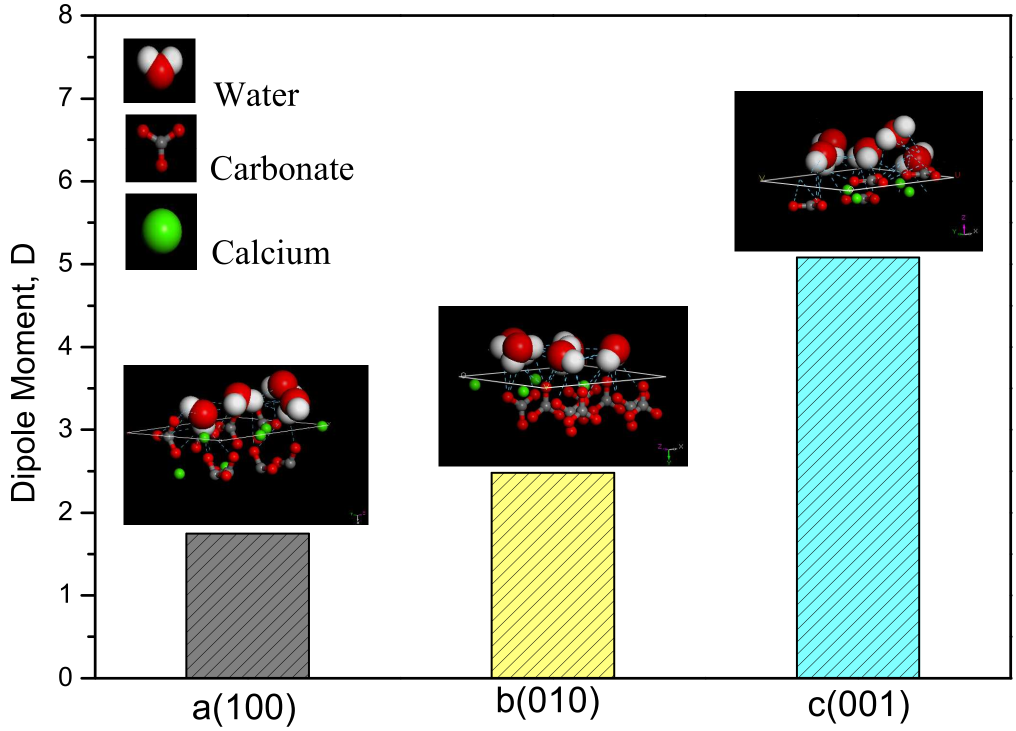


Figure 5. A proposed mechanism for the growth of aragonite particles.

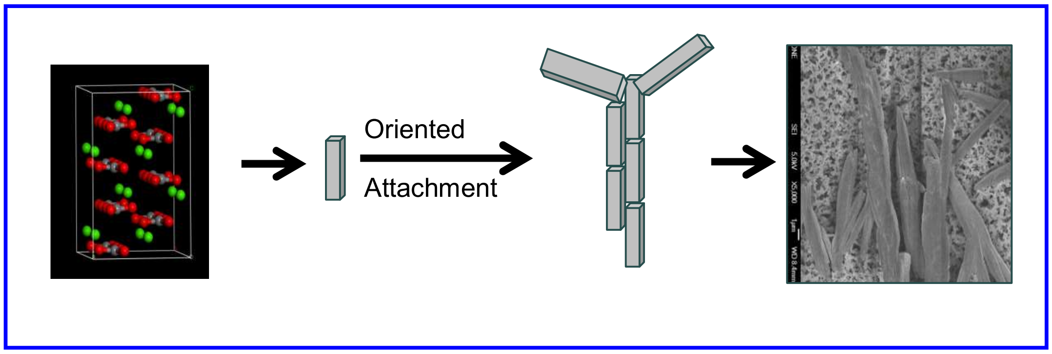


Figure 6. A compromise in competition between attractive force and destructive force leading to the variation of aragonite structure with temperature.

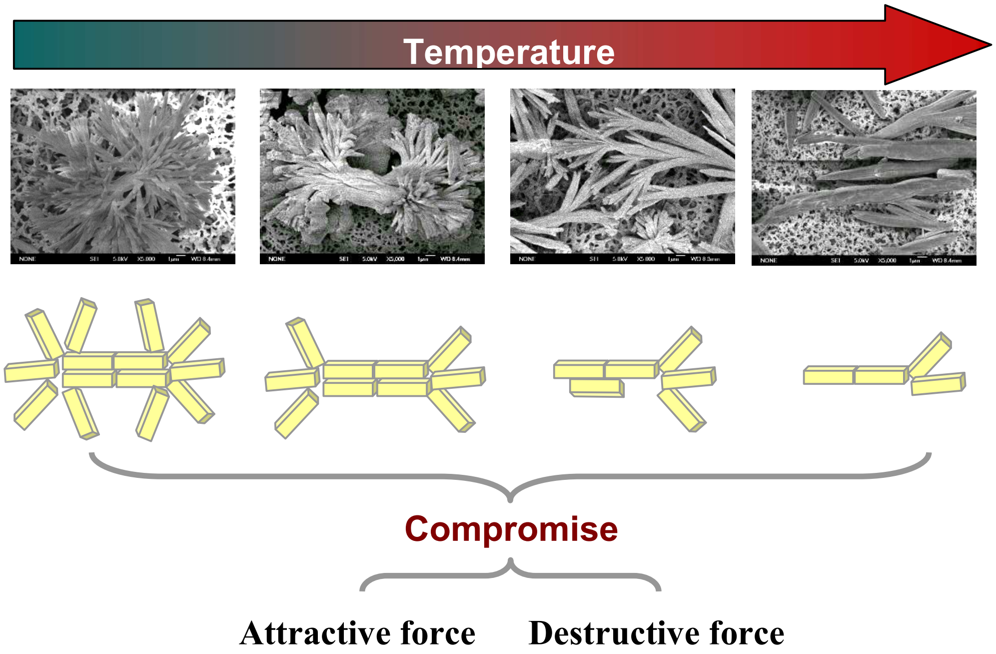


Figure 7. Illustration on the adsorption of water molecules on the surface of the aragonite crystallite. (a) Water molecules are randomly distributed around the aragonite crystallite; (b) Water molecules are bound on the surface of aragonite crystallite.

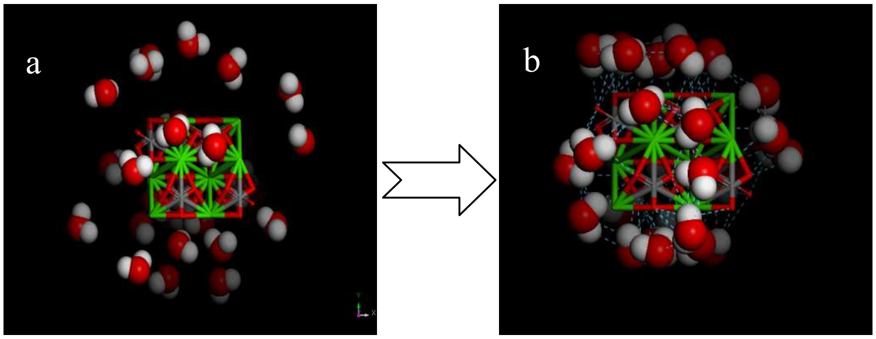
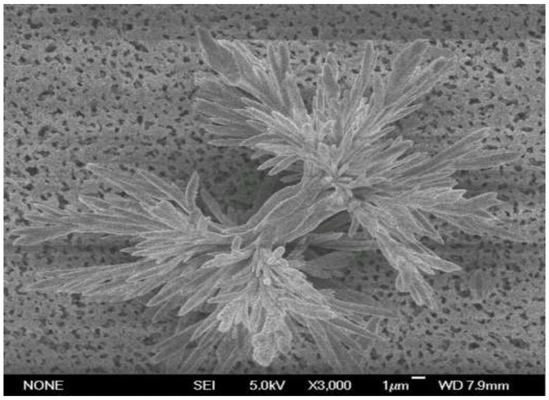


Table of Contents



A compromise between competing forces dominates the diversity of material structures.