A Unified Description of Attachment-Based Crystal Growth

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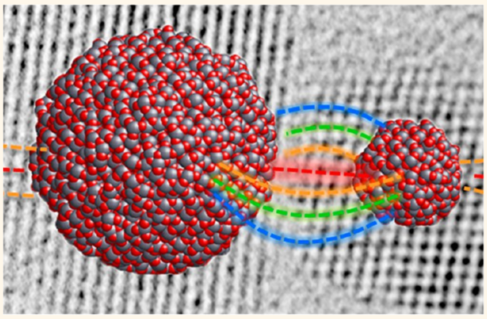

ABSTRACT Crystal growth is one of the most fundamental processes in nature. Understanding of crystal growth mechanisms has changed dramatically over the past two decades. One significant advance has been the recognition that growth does not only occur atom by atom, but often proceeds *via* attachment and fusion of either amorphous or crystalline particles. Results from recent experiments and calculations can be integrated to develop a simple, unified conceptual description of attachment-based crystal growth. This enables us to address three important questions: What are the driving forces for attachment-based growth? For crystalline particles, what enables the particles to achieve crystallographic coalignment? What determines the surface on which attachment occurs? We conclude that the extent of internal nanoparticle order controls the degree of periodicity and anisotropy in the surrounding electrostatic field. For crystalline particles, the orienting force stemming from the electrostatic field can promote oriented attachment events, although solvent-surface interactions modulate this control. In cases where perfect crystallographic alignment is not achieved, misorientation gives rise to structural defects that can fundamentally modify nanomaterial properties.

KEYWORDS: particle-mediated growth · oriented attachment · oriented aggregation · particle orienting force · electrostatic field · aggregation driving force · amorphous particle

Aggregation-based pathways of crystal growth are now recognized as pervasive in a wide variety of natural and synthetic environments. Aggregation of amorphous particles is a fundamental step in creation of many crystalline biominerals, which often have highly complex morphologies.[1−14] Subsequent to aggregation, interface elimination and recrystallization are thought to occur in the absence of true solution, resulting in crystalline products. Oriented attachment (OA), a crystal growth pathway that involves aggregation of crystallographically oriented discrete particles followed by interface elimination (Figure 1a,b), has been invoked for a wide range of nanomaterials[15−19] and mineral systems.[20,21] It can give rise to particles with unusual morphologies, with shapes not predictable from the symmetry of the bulk material. The fact that OA occurs was deduced on the basis of morphological information obtained from crystal growth experiments.[22] Full acceptance of the pathway awaited direct visualization of the process at high resolution in transmission electron miscroscope (TEM) fluid cells.[23]

Driving Force for Oriented Attachment. The major driving force for all aggregation-based crystal growth comes from surface energy reduction, which was initially identified as the key factor in selection of the attachment surface during OA based on the observation that OA frequently occurs on high-surface-energy faces.[15,16] However, surface charging of particles produces electrostatic repulsion that hinders OA. These two opposing forces are pH dependent because the magnitudes of both the surface energy and surface charge depend on pH. Moreover, an accurate description of the energy change during the entire OA process should include more than the elimination of the attaching surfaces. Interactions among all atoms within two attaching particles, both on the surfaces and in the particle interiors, contribute to the energy changes. On the basis of these considerations, it was shown that the overall potential energy of interaction (interaction energy), involving all atoms in the particles prior to and following attachment, provides a more complete predictor of the attachment surface.[9]

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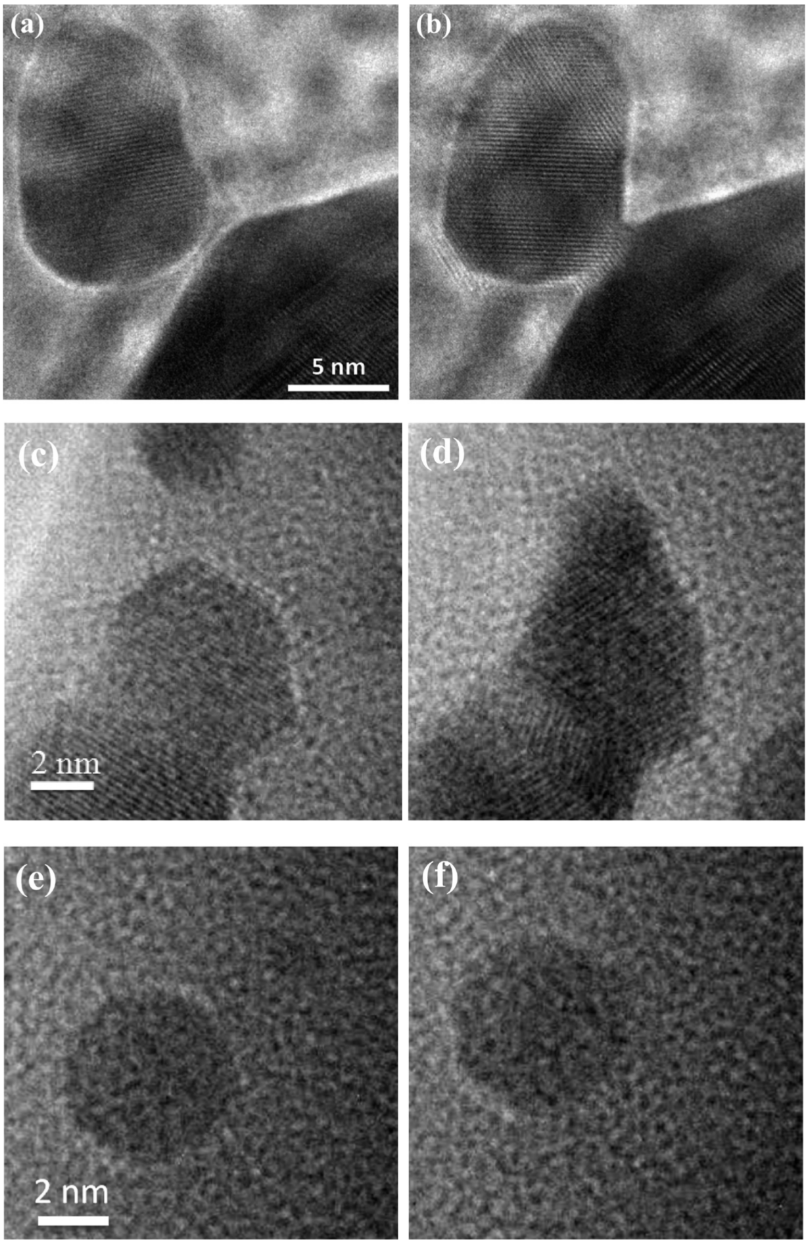

Figure 1. Aggregation events by crystalline and amorphous particles. (a and b) Oriented aggregation of two ferrihydrite nanocrystalline particles occurred after several intermediate rotational and translational movements of the smaller particle searching for an appropriate attachment orientation. (c and d) Aggregation of a smaller amorphous calcium carbonate particle to a bigger crystalline calcite particle. (e and f) Aggregation of a smaller amorphous calcium carbonate particle to a bigger amorphous calcium carbonate particle. (a and b) Adapted with permission from ref 23. Copyright 2012 American Association for the Advancement of Science. (c–f) Reprinted from ref 2 with the permission of Cambridge University Press. Copyright 2014 Microscopy Society of America.

Particle-Orienting Force Arising from Periodicity of Crystal Structure. Several lines of evidence point to atomic Coulombic interactions as the dominant control during particle–particle attachment, coming into play primarily when particles approach each other closely.[9,10,23] But what ensures that particles achieve crystallographic coalignment prior to interface elimination? The existence of an orienting force is likely required, and at least in the case of ferrihydrite, direct observations of angular accelerations during OA demonstrate its presence.[23] In the case of particles with high degrees of internal order (*e.g.*, 3–5 nm diameter ZnS or TiO_2 nanoparticles), we suggest that the orienting forces arise because of a degree of periodicity in the electrostatic (Coulombic) field surrounding the particle (Figure 2A). It makes sense that the field is periodic because the field arises from all of the atoms in the particle, and they are (mostly) periodically arranged. Some evidence for such a field can be found in molecular simulations that predict periodicity in water structures around nanoparticles[24] (Figure 2), and recent atomic force microscopy studies have directly documented the

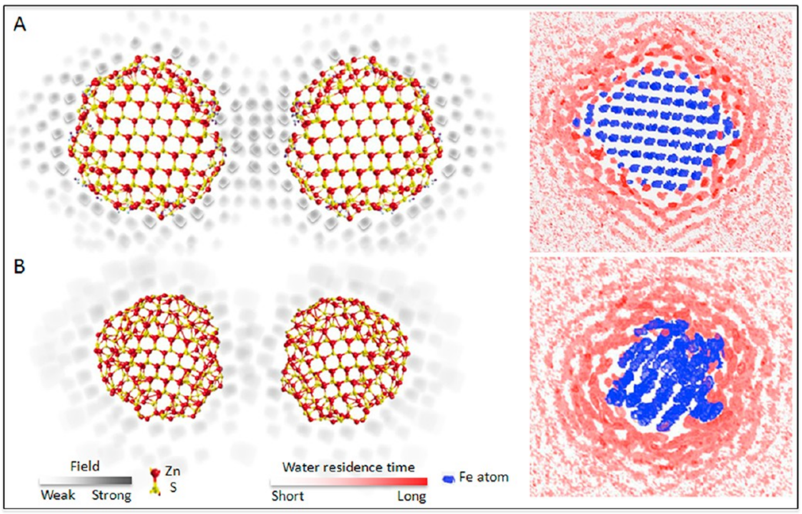

Figure 2. Conceptual diagrams illustrating the fields around nanoparticles in aqueous solution that give rise to an orienting force (left panel) and influence the distribution of surrounding water molecules, as calculated by molecular dynamics simulations by Spagnoli *et al.*[24] (right panel). (A) Larger, more ordered particles. (B) Smaller, less ordered particles. Note the prediction of a more ordered field around more crystalline particles, increased field periodicity in between oriented particles, and the expectation of increased order with nanoparticles due to particle–particle interactions. Periodic water structure at mineral surfaces has also been detected directly by atomic force microscopy.[25] Right panel reprinted with permission from ref 24. Copyright 2009 Elsevier.

periodicity of water structure near crystal surfaces.[25]

Particle Coalignment Driven by the Orienting Force. For crystalline materials, internal structure is direction-specific and the field strength normal to nonequivalent surfaces could differ significantly. When two particles approach one another, the field of each elicits a direction-specific structural response from the other that further alters these fields, creating a final interaction potential that is also direction-specific. The anisotropic gradient of the interaction energy should then drive the particles to co-orient. The direction that gives rise to the largest decrease in overall energy following OA will have the strongest average field gradient. This should drive OA on the specific attachment surfaces that yield the lowest overall energy,[9] as is typically seen.[2,23]

Propagation of OA Events Driven by Overall System Energy. In cases where an OA event has occurred, the field surrounding the nanoparticle will arise from all of the atoms in the resulting particle. If attachment gives rise to a crystal with morphology typical of a material of lower symmetry than that of the primary particle, the field will also have lower symmetry. The field strength along the direction of the first attachment event *may* be significantly higher than in any direction inclined to it, driving sequential attachment events along that direction. However, in other cases, the strongest field may not coincide with this attachment direction, leading to sequential attachment events on distinct crystallographic faces that can even alternate back and forth.[9,18] In general, the direction of the strongest field between the two particles should control the direction of subsequent attachment events. The connection between overall atomic structure following attachment and the consequent evolution of the electrostatic field characteristics provides a reason the energetic calculations can correctly predict the geometry of sequential attachment events.[9]

All aggregation-based growth of particles with internal order can be described within a single framework, with differences in the degree of crystallographic alignment giving rise to a variety of defects.

Now, we turn our attention to the question of how particles seem to know that if they attached on a different pair of surfaces than the ones on which OA occurs, the net reduction in overall energy would be smaller. The explanation may again relate to the magnitude and structure of the electrostatic fields normal to different surfaces. If the interaction is weak for particles approaching along a certain direction, attachment may not occur, or it may occur at a low frequency compared to attachment on surfaces for which the interaction is stronger. An interesting case may be if an incoming particle experiences the field asymmetrically: part of the approaching particle feels a weak interaction but another part feels a stronger field. This could cause the particle to rotate or to move toward an alternative surface prior to attachment.

Imperfect Particle Attachment Leads to Defect Formation. In some cases, attachment does not involve perfect crystallographic alignment of particles (Figure 3). Such events

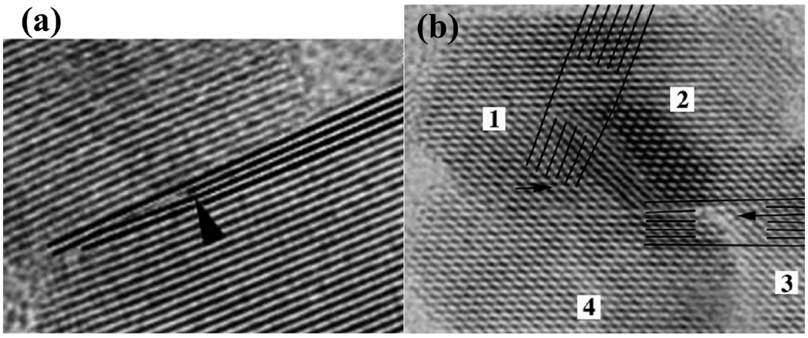

Figure 3. (a) High-resolution transmission electron microscope (HRTEM) image of two attached anatase particles showing the presence of an edge dislocation at the attaching interface. (b) HRTEM image (recorded down [100] anatase) of a portion of an anatase crystal formed by oriented attachment of at least four primary anatase particles. Arrowheads and lines (spaced 0.48 nm apart) indicate edge dislocations. Reprinted with permission from ref 15. Copyright 1998 American Association for the Advancement of Science.

can give rise to dislocations.[15,23] Events that achieve coherence in the interface but do not involve three-dimensional (3D) structural accord result in twins and stacking faults.[23,26,27] Finally, there are cases where nanoparticles with internal order attach in very different orientations. This results in 3D defects, also described as grain boundaries.[2,28] Thus, all aggregation-based growth of particles with internal order can be described within a single framework, with differences in the degree of crystallographic alignment giving rise to a variety of defects.

> Seemingly distinct processes involving aggregation-based growth of amorphous and crystalline particles, and oriented and misoriented attachment can be described as part of a continuum associated with a single growth pathway.

Attachment of Particles with Little or No Long-Range Structural Order. Consider now the case when the particle has low internal order. We expect the surrounding field will be less periodic than that around an ordered particle (Figure 2B). The orienting force would thus be quite weak, although OA may occur. It should be noted that particle structure is itself a function of the environment (*e.g.*, solvent type[29]) and the degree of internal order can increase as particles approach due to interatomic interactions that are evidenced even without interface elimination.[30] This may increase the probability of OA-based growth in small disordered particles. Finally, a particle may have so little internal order that it is considered amorphous and attachment, thus, cannot be described as oriented (Figure 1c–f). However, even for amorphous particles there will be a surrounding field that may promote particles to adopt favorable configurations prior to the attachment step. Overall, it is reasonable to describe aggregation of particles with all possible degrees of internal order within a single attachment-based framework.

Effect of Surface Environment on Particle Aggregation. An aspect not considered above is the contribution of the energy associated with surface-bound molecules (and/or ions) to the overall energy of the system. For example, if an OA event occurs in aqueous solution, the net change in energy includes a contribution from surface-bound water molecules, and this will be surface specific. This contribution will also be a factor for particles with little or no internal order. An easily appreciated case involves two hydrophobic surfaces, where the decrease in energy due to water desorption upon attachment may be a larger contribution to the decrease in energy than would be the case for attachment of two hydrophilic surfaces. The contribution of hydration energy to the overall energy change upon interface elimination may be large enough relative to the driving force arising from particle–particle Coulombic interactions to impact selection of an attachment surface. This effect may also manifest as a kinetic phenomenon, where the rate of attachment is slow on surfaces with large dehydration energies, even if attachment on those faces would lead to the lowest overall system energy. Recent molecular dynamics simulations showed that, for anatase nanocrystals, OA is dominant on surfaces that have high propensities to dissociate water molecules.[11] This was ascribed to the need for the formation and removal of hydrogen bonds between two attaching surfaces, which would facilitate the attachment kinetically. Because the influence of surface-bound species on the attachment process can be modulated by solution chemistry, the presence of these barriers (due to surface desorption/dehydration/dissociation) opens up multiple routes for control of attachment-based growth.

SUMMARY AND CONCLUSION

Seemingly distinct processes involving aggregation-based growth of amorphous and crystalline particles, and oriented and misoriented attachment can be described as part of a continuum associated with a single growth pathway. Where along that continuum a particular nanoparticle system lies is related to the variability in the strength and anisotropy of the field gradient associated with the particle−particle interaction potential. In addition, the role of solvent−surface interactions, both as a factor in determining the strength of attraction and the barrier to attachment, cannot be ignored. We conclude that a predictive understanding of attachment-based crystal growth and its consequences is achieved when internal nanoparticle order is identified as a key parameter and the degree of periodicity and anisotropy in the surrounding electrostatic field as major controls.

Conflict of Interest: The authors declare no competing financial interest.

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