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# Understanding the Influence of Crystallographic Structure on Controlling the Shape of Noble Metal Nanostructures

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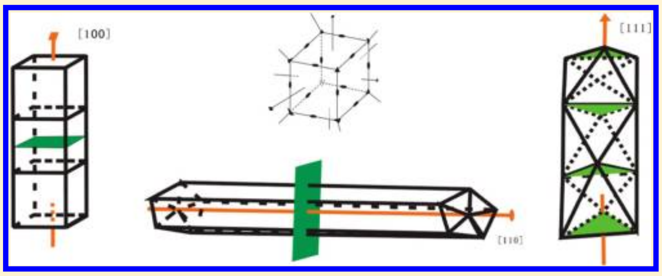
S *Supporting Information*

**ABSTRACT:** Although internal features of a crystal play key roles in crystal growth, the relationship between crystal structure and crystal shape is still an unresolved problem. In this paper, we constructed a correlation between crystallographic structure, morphological evolution, and resultant final shape of noble metal nanocrystals. The minimal stable crystal was predicted to consist of 27 unit cells, which facilitates the growth of the crystal matrix into different shapes. During the parallel grouping process, anisotropic nanocrystal with thermodynamically unfavorable shapes was observed via the symmetry axis and symmetry facet. The results indicate that the formation of isotropic shapes with single or multiple twinned crystal structures are still governed by the internal order of crystal structure.



## 1. INTRODUCTION

In recent years, extensive effort has been devoted to controlling the size and shape of nanocrystals from the view of both fundamental understandings and practical applications.[1−3] Among various nanoscale crystals, physical and chemical properties of noble metal nanocrystals are particularly sensitive to size and shape changes.[4−6] A diversity of synthetic methods have been developed in controllable production of isotropic and anisotropic nanostructures; however, the formation mechanism of the nanocrystals appears to be different in these cases. Crystals often present different shapes depending on various internal factors, such as crystallographic structure of crystal, and external factors, such as growth environments.[7,8] When examining a particular reaction environment, mainly two mechanisms have been proposed to explain the crystal growth. In one case, organic molecules are introduced into the growth solution, which interact with specific crystal faces and modify the relative growth rate of different crystal facets.[9,10] The other mechanism describes high concentrations of surfactants in micelles, which act as templates for crystal growth.[11,12] In terms of high symmetry materials, some other explanations have been addressed as well.[13,14] Recently, it was shown that symmetry-breaking and the concave sites formed between twin planes could overcome the point group symmetry and form nanocrystals with thermodynamically unfavorable shapes.[13−16] There is a close relationship between shape and internal features of a crystal, but it still remains unclear what roles these internal features of the crystal play in crystal growth and shape change, especially in the aspects of the crystallographic structures of the crystals. (These internal features include point groups and space groups, which correlate to morphology and lattice of crystals, respectively). Herein, we intend to create a correlation between the morphology evolution and the nature of the crystal, as well as the resultant zero- and one-dimensional nanostructures. Using crystallography to understand morphological evolution makes it possible to understand the variations in shape of crystals that are obtained during synthesis.

## 2. PREDICTIONS OF THE THEORETICAL MODEL

In general, a crystal is described as a homogeneous solid possessing long-range, three-dimensional internal order.[17−19] In principle, a crystal exhibits six unchangeable features: self-restriction, homogeneity, anisotropy, symmetry, minimum internal energy, and stability. The crystal structure of noble metals forms using the cubic face-centered (*fcc*) lattice as a unit cell, which belongs to the *m3m* point group and the *Fm3m* space group (Figure S1, Supporting Information). The unit cell possesses four atoms that, due to the interplay of attractive and repulsive forces, pack together into the smallest volume possible. The direction in which the close-packed (*cp*) layers stack, called the packing direction, lies along the body diagonal of the unit cell. A number of experiments have demonstrated that different crystal

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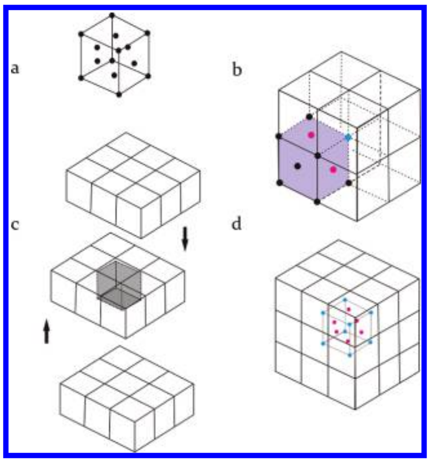

**Figure 1.** Minimum crystalline particle. (a) A *fcc* lattice. The black balls are activated atoms. (b) some atoms of *fcc* lattice are conjugated with neighboring unit cells. The red and blue balls represent the stable atoms which belong to the corner and facet, respectively. (c) Twenty-seven unit cell stacking. (d) The central lattice is stable. All atoms of this unit cell are completely stable.

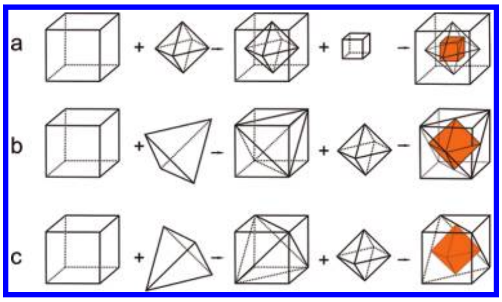

**Figure 2.** Crystallography geometric relations between cube, tetrahedron, and octahedron. (a) Cube and octahedron, (b) cube, plus-tetrahedron, and octahedron, and (c) cube, minus-tetrahedron, and octahedron.

shapes can be obtained by adjusting external factors, such as temperature, surfactant, or supersaturation.[6,20−22] However, no matter what the reaction conditions are, these rules of crystal structure still govern their external shape.

**2.1. The Size of Minimum Particle.** Since crystals are built by the periodically ordered accumulation of unit cells in three-dimensional space, a lattice unit cell instead of single atom should be considered as the fundamental unit for crystal growth. The atoms located at the corners and the centers of the faces identify to which layer of the cubic closest packing it belongs. There are three possible packing layers (identified as A, B, or C) that can be expressed as an ABCABC... sequence following the $L^3$ axes. The minimum crystal has at least one stable lattice unit cell, that is, all the atoms of this unit cell must be stable. Figure 1 shows a schematic illustration indicating the minimum crystal built from 27 unit cells. The atoms located on the corners and facets are conjugated with seven and two neighboring unit cells, respectively. Thus, the unit cell is surrounded by an additional 26 unit cells. It is then possible for the crystal matrix to grow into different shapes, including cubes, octahedra, tetrahedra, or other shapes. For example, the minimum cube of silver crystal consists of 27 unit cells that are the arrayed periodically in a three-dimensional infinite space. On the basis of the cell parameters of silver ($a = b = c = 0.4086$ nm, $\alpha = \beta = \gamma = 90°$), the size of silver nanocrystal thus obtained is 1.2258 nm on each side and 1.8419 $\text{nm}^3$ in volume.

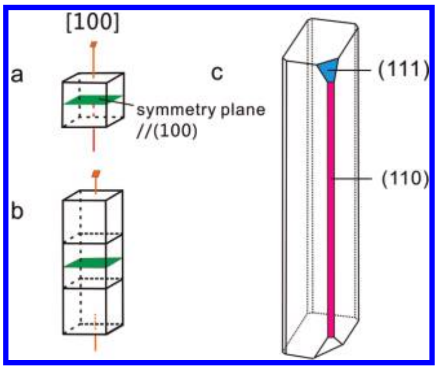

**Figure 3.** Single crystal nanowire. (a) The symmetry plane (green) is vertical to the $L^4$ axis. (b) Cube stacked along the [100] direction. (c) Long single-crystalline nanowire is truncated by (111) and (110) facets.

Although noble metal crystals invariably present as different shapes, they have a fcc lattice and the *Fm*3*m* space group, as revealed by X-ray diffraction and high-resolution transmission electron microscopy.[6,23,24] Cubes, octahedra, and rhombic dodecahedra all belong to the *m*3*m* point group with the same symmetry. Tetrahedra are also present in the structures that belong to the $\bar{4}3m$ point group, which is the subset of *m*3*m* point group with same crystal system (isometric). Due to this primary and secondary relationship, these polyhedra can combine with each other. Figure 2 shows the geometric relationships in crystallography. In addition, as crystal growth is an ongoing process, truncation is a common phenomenon and affects the edge, corner, and angle locations in the resulting crystal.[23] Cuboctahedra and truncated octahedra are representative combinations of octahedra derived from cubes.[24] Different isotropic particles with truncated facets are also observed, and these shapes must also be consistent with the intrinsic symmetry of crystals. Cubes and octahedra can even be so truncated as to form each other. Tetrahedra are often truncated by themselves as two tetrahedra can form from the same cube (the "plus−minus" tetrahedron, Figure S2, Supporting Information). This makes experimental products consist of a mixture of these three polyhedra, even when the reaction environment is highly homogeneous.[13]

**2.2. Anisotropic Growth.** It is well-known that anisotropic shapes are uncommon in *fcc* crystals because the high symmetry limits the possible shapes. Fortunately, inherent crystallographic anisotropies are present along the [111], [100], and [110] directions, which provide potential growth directions. Generally, the morphology of noble metal crystals is often determined by particular facets under nanoscale, such as octahedra with (111) facet, tetrahedra with (111) facet, cube with (100) facet. These facets have the high network density, which meets the Bragg rule. By adjusting the chemical conditions, this growth trend can be accelerated and/or decelerated, giving rise to various anisotropic nanostructured crystals.

*2.2.1. Single-Crystalline Nanostructures.* Nanorice, nanobar, and nanorod with single-crystalline nanostructures are a class of anisotropic materials that are short and truncated to different degrees. Cubic structures have the highest symmetry, and have symmetry axes, planes, and centers ($3L^4 4L^3 6L^2 9PC$) that are the same as the original unit cell. One-dimensional nanostructures are supposed to be readily constructed via parallel grouping processes. Figure S3a (Supporting Information) shows the atom

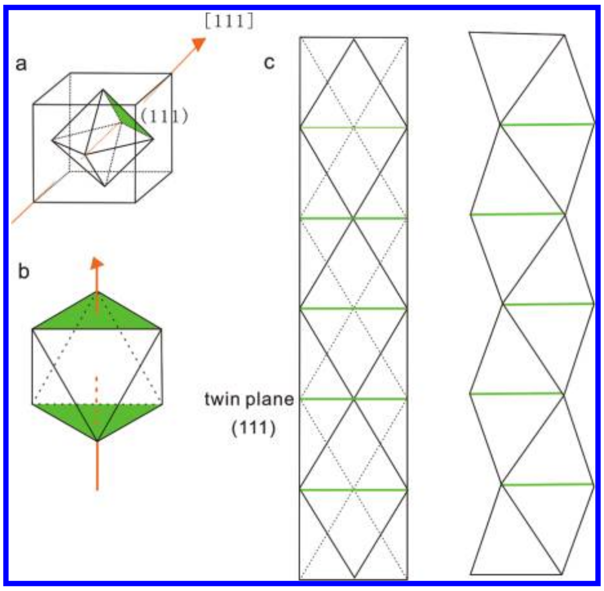

**Figure 4.** Twinned crystal nanowire. (a) The relationship of cube and octahedron. (b) $L^3$ axis is vertical to (111) facet, which is the twin plane. (c) Octahedron are attached along the [111] direction by (111) twin planes.

**Table 1. Position of the Atomic Layer**

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ··· | A | B | C | A | B | C | B | A | C | B | A | B | C | A | B | C | ··· | → [111] |
| ··· | h | c | c | c | c | h | c | c | c | c | h | c | c | c | c | h | ··· | → [111] |
| | ‖ | | | | | ‖ | | | | | ‖ | | | | | ‖ | | ‖ twin-plane |

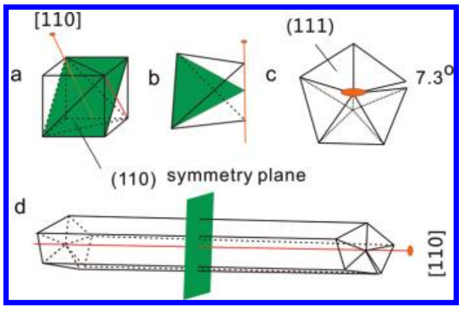

**Figure 5.** Multiply twinned nanowire with 5-fold axis. (a) The edge of tetrahedron is parallel to the $L^2$ axis and vertical to the symmetry plane, which is the (110) facet. (b) $L^2$ axis is vertical to the plane. (c) Decahedron formed with 5-fold axis along the [110] direction. (d) Decahedron is elongated to multiply twinned nanowire by a parallel grouping process.

arrangement in $L^4$. The growth direction of crystal is vertical to (100) plane, parallel to the $L^4$. Since the symmetry plane [(100)] is perpendicular to the growth direction ([100]), the crystal could be considered to be a series of cubes stacked together in a specific direction assisted by external factors (such as surfactant), giving a single crystal without twinning. Because the (100) plane is only one of the three possible stacking planes for crystal growth, additional growth along other directions always exists in forming a real crystal. Figure 3 shows the steps of the cube grown into the nanorod with the (111) and (110) truncation. Conversely, tetrahedra and octahedra are also often truncated at the (100) facet for these polyhedra because of a very similar internal order. Once truncation occurs, the difference of surface energies between the facets restricts continued growth of the crystals along the $L^4$ direction. Different network density of (111), (100), and (110) facet can lead to different growth rate of the facet, and truncation often occurs in the formation of final crystals. These truncations would restrain the crystal growth from growing into long nanowires because the facets with high network density always grow faster than the facet with low network density. So it is difficult to grow the single one-dimensional nanostructures into long nanowires.

*2.2.2. Twinned-Crystalline Nanostructure.* One-dimensional nanostructures also could be attached by twinned-crystalline nanoparticles.[6,25−27]For example, the ultrathin gold nanowires with twinned-crystalline nanostructures, which have been formed by the oriented arrangement of octahedra along the [111] direction. Compared with the other two polyhedra, octahedra with covered (111) facets are the closest to spherical with the highest symmetry axes and maximum crystal facets (not symmetry plane), which favors the packing. Figure S3b (Supporting Information) shows the atom arrangement in $L^3$. The packing direction is perpendicular to the (111) facet and does not have a symmetry plane, producing the twin plane when two octahedra came into contact along this direction. The octahedra can pack efficiently by rotating 120° as the $L^3$ lies parallel to the [111] direction. As the octahedra arrange periodically in this direction through a series of contact twins, a multiply twinned crystal is formed as a linear array through the (111) facet with the convex and concave regions on either side. In this case, the highest symmetry axis in the growth direction is $L^3$ instead of $L^4$. These wires contain two types of close packing: it is cubic close-packed for each octahedron; the atoms of the third layer have two optional positions where they can be located in the set of indentations of the second layer (the B layer). They can either be directly above the first layer (the A layer) or not directly above the first layer by forming a C layer. Continuation of the second option gives the sequence ABCABC.... The atoms are arranged the same way as that in a cubic face-centered cell. Hexagonal close packing occurs between the octahedra with twin planes, where the atoms of the third layer are directly above those in the first layer to give an ABA sequence. Continuation of this sequence ABAB... gives a structure known as hexagonal closed packing structure. Figure 4 shows nanowires formed by the stacking of octahedra. In Table 1, *h* is the (111) facet of octahedron, which is also the twin plane.

*2.2.3. Multiply Twinned Crystalline Nanostructure.* Five-fold nanowires are a distinct kind of one-dimensional nanostructure, which are formed from multiply twinned nanoparticles (decahedra). The ends of the nanowires are terminated by (111) facets with near-5-fold symmetry, and the sides are bounded by (100) facets. The impossibility of forming particles with 5-fold symmetry axes was demonstrated previously;[28,29] however, the mechanism is still questioned in terms of constructing nanowires. As tetrahedra have relatively low symmetry with lower symmetry axes ($3L_i^4 4L^3 6P$) and without symmetry center, it is difficult to form one-dimensional nanostructures by simply parallel grouping. During initial crystal growth, twinned nucleation is more stable, as two tetrahedra can share one facet, which efficiently decreases the interfacial energy. The first two tetrahedra came into contract along the packing direction ($L^3$) and produced a twin plane. As the crystal grows, nanowire cannot be formed, but the cyclic twinned crystal forms from five tetrahedra stacked together with both shapes exclusively bound by the (111) crystal facets because of the polar tetrahedra.

The edges of the twin plane, which lies on the face diagonal of a cube, are parallel to the $L^2$ ([110] direction) of the cube. In this direction, and the $L^2$ axis is perpendicular to the (110) plane. When $L^2$ is rotated and parallel to the near-5-fold axes of the multiply twinned nanoparticle, each tetrahedron of the five-twinned crystal grows along the $L^2$ axes to form a near-trigonal prism, without a twin plane, by parallel grouping because the $L^2$ axes is perpendicular to the (110) symmetry plane. Thus, decahedral particles appear as five near-trigonal prisms, joined to each other by a single plane, and giving a multiply twinned nanowire. Figure 5 shows the relationship between the near-5-fold symmetry of the multiply twinned crystal and the $L^2$ of a single tetrahedron.

## 3. CONCLUSION

Our analysis shows that the internal structure of a crystal is critical to understand the various shapes of noble metal crystals and can be applied to understand the nature of crystal growth. In principle, it is possible to extend this crystallographic description to explain a large range of noble metal nanostructures with different morphologies, including core−shell structure and bi-metallic structure. We expect that the new insights into the general rules of crystal growth can help predict the shapes of crystals based on the nature of the underlying crystal structure.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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