Shape variations and anisotropic growth of multiply twinned nanoparticles

Herbert Hofmeister*

Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Received May 27, 2008; accepted September 21, 2009

Electron microscopy / Crystal morphology / Shape evolution / Multiple twinning / Pseudofivefold rotation / Anisotropic growth

Abstract. Cyclic multiple twins as nanoobjects that display nearly regular polyhedron shape variety together with strongly anisotropic shape variations due to growth processes are reviewed with regard to their unique shape evolution based on the specific formation modes as well as on the particular structure of twin-related subunits. The review includes (i) the shape variations due to growth by stacking of tetrahedral subunits, (ii) the role of growth conditions in the shape evolution of multiply twinned nanoparticles, and (iii) the modes of twin-based anisotropic growth including branching growth and unidirectional growth. The particular structures are introduced making use of electron microscopy structural characterization of multiply twinned metal nanoparticles as well as some non-metal examples, and instructive models of the various configurations.

1. Introduction

1.1 Shape evolution of nanoparticles – the role of twinning

Nanoparticles with strong shape anisotropy, like rod or platelet shapes, attract large attention because of their interesting physical properties. For single crystalline particles there is a lot of methods to achieve strongly anisotropic growth (see, e.g., [1–5]). Sources of anisotropic growth may be either the position within the growth environment which can lead to anisotropic shape of crystallites having equivalent faces, or differences in growth rate of crystallites bounded by different faces where the growth rate ratio is depending on temperature and supersaturation. In view of more complex routes of synthesis anisotropic growth of one-dimensional nanostructures may occur, for example, as unidirectional axial growth due to inhibition of radial growth. Such growth techniques may be classified as seed-mediated, template-directed, or defect-mediated growth, respectively [5].

Quite different, but not less remarkable shape variations can be found for multiply twinned particles (MTPs) with non-crystallographic pseudo-fivefold rotation axes, that means particles with decahedron and icosahedron shape [6, 7], respectively. Cyclic fivefold twinning is a widespread habit of nanoparticles [7], found not only in synthetic materials as reported for the first time in 1957 [8], but also in crystallite compounds of natural origin, dating back as early as 1831 [9]. For the sake of clarity we should consider all these twins as being due to pseudo-pentagonal metrical features of the corresponding lattice. Thus they actually are pseudo-fivefold rotation twins [10]. Besides the classical processes of nucleation and growth, at MTPs also shape evolution by successive stacking of tetrahedron-shaped subunits arranged around fivefold rotation axes has experimentally been observed. The shape variations of multiple twins with nearly regular polyhedron shape can mostly be explained by different growth rates of the bounding faces of their subunits, if they do not exhibit tetrahedron, but cuboctahedron shape. Then star decahedron, prism, facet, and cube decahedron, respectively, may occur as corresponding growth forms.

At particles with decahedron shape a strongly anisotropic shape evolution may proceed by preferred growth along one or some reentrant edges of the outer bounds of twin planes or along the fivefold junction. While the former results in radial growth in one or some directions, the latter is equivalent to unidirectional axial growth due to an inhibition of any radial growth. The rod shape formed thereupon corresponds to a pentagonal prism with pentagonal pyramids at the rod tips [11]. At particles with icosahedron shape strongly anisotropic shape evolution is mainly observed via preferred attachment of tetrahedron-shaped subunits along a fivefold axis, through which stacks of pentagonal antiprisms with pentagonal pyramids at the rod tips may form [12].

The above mentioned shape variations as well as examples of strongly anisotropic growth of MTPs shall be introduced by means of electron microscopy findings of our own work including various collaborations, as well as some work reported in the literature, and shall be illustrated by appropriate models. The materials involved comprise noble metals and semiconductors, as well as molecule crystals and even a silicate mineral. Besides a short introduction of composition and appearance of multiply twinned particles, this review contains considerations of...
1.2 Composition and appearance of multiply twinned particles of regular polyhedron shape

Multiply twinned particles consist of several subunits, that means they are composed in such a way that subunits of equal shape of regular tetrahedra are twin-related to each other resulting in polyhedra of unique morphology and unusual symmetry [7] as can be seen in the schematic representation given in Fig. 1. The one on the left hand side (Fig. 1a) is a decahedron, that means an equal edge length pentagonal bipyramid, containing 5 tetrahedra in contact twin orientation to each other stacked around one fivefold axis that is marked by a dotted line. The other one (Fig. 1b) is an icosahedron, that means an equal edge length, pentagonal antiprism pyramid-capped on both sides, containing 20 tetrahedra, also in contact twin orientation to each other, stacked around six fivefold axes which are marked by dotted lines. Their mode of appearance depends on the orientation with respect to a supporting substrate or a surrounding matrix – four high symmetry orientations are known for both of the twin polyhedra [7] which are shown in Fig. 2 (decahedron) and Fig. 3 (icosahedron) where the indices refer to the directions [110] of a fivefold twin junction, [112] of a twin boundary, or (001) of a tetrahedron subunit parallel to the viewing direction, or to the direction [111] of a bounding face of a subunit perpendicular to the viewing direction. The resulting particle images have rhombic, pentagonal or hexagonal contour of various style.

2. Shape variations due to growth by stacking of tetrahedral subunits

Previous to any shape variation of the multiply twinned polyhedra, elementary steps of shape evolution occur via

Fig. 1. Schematic representation of a decahedron (left) and an icosahedron (right) composed of regular tetrahedra arranged around fivefold axes.

Fig. 2. Schematic drawing of the appearance of decahedra in high symmetry orientations on a substrate.

Fig. 3. Schematic drawing of the appearance of icosahedra in high symmetry orientations on a substrate.

Fig. 4. Successive stacking of tetrahedra via repeated twinning during growth illustrated by (a) schematic drawing, and (b) TEM images, adapted with permission from [14], in bright-field (upper row), and dark-field (lower row) mode of one, two, and three subunits.
assembling of tetrahedra subunits by repeated twinning during growth. This successive stacking of subunits easily results in the formation of decahedra, and icosahedra, respectively [13–15], as it is demonstrated in Figs. 4 and 5 for decahedra and in Figs. 6 and 7 for icosahedra. The experimental observation of the first steps shown in Fig. 4b includes transmission electron microscopy (TEM) images in bright-field (upper row) and in dark-field (lower row) mode of an unattached tetrahedron in (001) orientation (left) as well as particles containing one and two twins attached to a parent subunit (centre and right) as it is schematically sketched in Fig. 4a [14]. In principle, the assembling of five individual tetrahedra so as to form a decahedron as indicated by Fig. 5 cannot be excluded. The process of subunits assembling obviously does not stop with creating decahedra, but continued stacking of subunits towards creation of icosahedra via intermediates containing eight and twelve tetrahedra as it is schematically drawn in Fig. 6 has been observed. Almost half-icosahedral particles obtained by physical vapour deposition (PVD) have repeatedly been reported as intermediate stage of the successive stacking of twinned subunits [14–18].

An experimental example of Gao et al. [15] from the solution growth of silver particles studied by scanning electron microscopy (SEM) is presented in Fig. 7 where a number of incomplete MTPs, including a three tetrahedra precursor of a decahedron and a 15 tetrahedra precursor of an icosahedron, are marked by arrows. Another route to icosahedra is modelled in Fig. 8 where a decahedron (left) is added to a pentagonal antiprism (centre) composed of ten twinned tetrahedra so as to create an intermediate stage (right) that needs another five subunits of a decahedron to end up with an icosahedron. The assembling of multiply twinned particles from tetrahedra subunits step by step implies that under certain conditions for the materials involved the tetrahedron may be a possible growth shape, at least during growth twinning at the nanometre scale. Usually, such materials have cubic crystal symmetry which can be grown into cubic, cuboctahedral, and octahedral shape, respectively, depending on the growth conditions. As will be demonstrated below, the latter modes of shape may occur for the subunits of completed multiply twinned particles whose structure is governed by twinning during the initial stage of spontaneous nucleation.

![Fig. 5. Contact twin-related assembling of 5 tetrahedron subunits to form a decahedron.](image)

![Fig. 6. Continuation of successive stacking of tetrahedra beyond the decahedron (a). Intermediate stages of 8 subunits (b) and 12 subunits (c) complement one another to an icosahedron (d).](image)

![Fig. 7. SEM images of silver particles from solution growth (Gao et al., adapted with permission from [15]) demonstrating intermediate stages (incomplete MTPs) formed upon successive stacking of tetrahedra.](image)

![Fig. 8. Alternative route to the assembly of an icosahedron via attaching a tetrahedron-based pentagonal antiprism to a decahedron leaving space for another decahedron in mirror symmetry to the first one.](image)
3. Shape variations due to growth rate changes

The shape evolution from the octahedral to the cubic form of crystals involves intermediate forms like the truncated octahedron, the cuboctahedron, and the truncated cube. Their outline is determined by the ratio of cube faces to octahedron faces growth rates \( v_{100}/v_{111} \) [3] or more common by the growth parameter \( a = \sqrt{3v_{100}/v_{111}} \) [19].

Subunits of general cuboctahedral shape are thought to result from progressive and symmetrical removal of the corners of both starting polyhedra that are exposed to variations of the growth conditions. Consequently, distinct shape variations of MTPs originating from multiple twin formation at the initial stage of growth may evolve upon suitably controlling the growth conditions, which increases the number of varieties of nearly regular polyhedron particle shape. The growth parameter \( a \) is determined by conditions like the precursor concentration and the substrate temperature applied during growth. Since the shape of single crystals can be easily correlated to this parameter, at least in the range \( 1 \leq a \leq 3 \), we have chosen four specific values of \( a \) corresponding to characteristic stages of shape evolution [3, 7, 19]. These are the octahedron obtained for \( a = 3 \), the truncated octahedron for \( a = 2 \), the cuboctahedron for \( a = 1.5 \), and the cube for \( a = 1 \).

3.1 Evolution of the decahedron morphology

According to the above mentioned values of \( a \) and the corresponding single crystal shape unique examples of MTP shape occur which are shown for the decahedron in Fig. 9. Different from the regular decahedron composed of five regular tetrahedra being bounded by equilateral triangular faces of type \{111\} only (see 1.2), now the particle morphology is subdivided and contains bounding faces of different type and size [19–22]. The evolution of the nearly regular polyhedron shape variety of decahedra contains, starting from a perfect octahedron shape of subunits, (i) a star decahedron that exhibits 5 peripheral reentrant edge configurations (Fig. 9a), (ii) a facet decahedron obtained by truncation of the outer tips of the star decahedron so as to display \{100\} faces (Fig. 9b), (iii) a prism decahedron resulting from increased truncation where the \{100\} faces contact each other (Fig. 9c), and (iv) a cube decahedron corresponding to a perfect cube shape of subunits, where no \{111\} faces remain (Fig. 9d). The prism decahedron model, also named “Ino decahedron” [20] and the facet decahedron model, also named “Marks decahedron” [21] have been introduced to take account of the necessary energy balance, mainly between surface and strain energy of these particles. Together with that of the regular decahedron, these decahedral particle shapes have been most frequently observed experimentally. From the experimental TEM images of a palladium decahedron, obtained by PVD on potassium iodide substrate, shown in bright-field and in dark-field mode in Figs. 10a and 10b one can clearly recognize its compact morphology [23].

Remarkably, the most earliest report on an object that exhibits multiply twinned configuration and decahedral shape is by G. Rose from 1831 [9] and it features, as can be seen from Fig. 11a, the subdivided morphology of a facet decahedron of gold which has been found near Boica, Romania. Another early example of natural origin [24] is the copper decahedron shown in Fig. 11b that exhibits peripheral reentrant edge configurations like a star decahedron, but no tips at the outer end of the subunits. Additionally, this particle displays a dimple at the emergence point of the fivefold twin junction, that means a concave vertex surrounded by five \{111\} facets. This morphological feature must not be considered as a characteristic of copper decahedra or decahedra of natural origin. There are also examples in the literature that describe a copper MTP of natural origin having clearly star decahedron shape without such central dimple [25], as well as diamond star decahedra of natural and of synthetic origin that just display this particular habit [26, 27]. The shape of the decahedron shown in Fig. 11b can be explained by assuming a truncated tetrahedron shape of its subunits. As illustrated by Fig. 12, stacking of such truncated tetrahedra, also known as Friauf polyhedra, easily enables to construct decahedra and even icosahedra [28] that exhibit both, twin junction dimpling and twin boundary grooving. Occasionally, a certain anisotropy of decahedral MTPs may occur because of non-uniform development of such features within the subunits of a particle as it is observed at the C60 star decahedron obtained by aerosol synthesis [29].

Fig. 9. Evolution of decahedron morphology with growth parameter affecting the subunit shape: (a) octahedron; (b) truncated octahedron; (c) cuboctahedron; (d) cube.

Fig. 10. TEM images of a PVD grown palladium decahedron with its twin junction oriented parallel to the electron beam: (a) in bright-field; and (b) in dark-field mode [23].
Dence of fabrication of a cube decahedron without any {111} faces is rarely found, but for values of the growth parameter slightly above $\alpha = 1$ reentrant grooving at the twin boundary sections between {111} faces occurs as it is schematically shown in Fig. 14a for $\alpha = 1.16$ [19]. This leads to additional cube faces at the expense of the still remaining octahedron faces.

Another direction of shape evolution is opened by the solution synthesis of gold nanoparticles using an eutectic mixture of choline chloride and urea as solvent that has been reported to result in star decahedra [30] whose tips are distinctly sharper than those bounded by octahedron faces as considered above. The free faces forming each tip are of the highly stepped {331} type resulting in a tip angle of $26.6^\circ$ instead of $70.53^\circ$ as expected for {111} faces. Obviously, this morphology is due to branching growth (discussed below in sect. 4.1) proceeding in direction of the apex of the octahedral subunits.

3.2 Evolution of the icosahedron morphology

The evolution of the nearly regular polyhedron shape variety of multiply twinned icosahedra is illustrated by Figs. 14b and 15. Changes of the subunit outline due to growth parameter variation produce different types of deviation from the regular icosahedron having a compact, nearly spherical shape. For subunits of octahedral shape the corresponding icosahedron is bounded by corner-connected, equilateral triangular faces of {111} type which always surround a pit, that means a concave pentagonal vertex consisting of {111} faces. As can be seen in Fig. 15a all these pits are corner-connected to each other. Smaller pits or dimples of the same geometry occur for subunits of truncated octahedron shape where the peripheral {111} faces now have hexagonal outline (Fig. 15b). A cuboctahedral subunit shape results in the morphology of a regular icosahedron not to be distinguished from that composed of tetrahedral subunits (see Fig. 15c). For values of the growth parameter $\alpha = 1.5$ twin boundary grooving occurs, as it is shown in Fig. 14b, whereby cube faces additionally appear at the expense of the diminishing octahedron faces. Finally, the multiply twinned icosahedron for $\alpha = 1$...
(Fig. 15d) can be described as regular icosahedron whose triangular bounding faces are capped by fitting pyramids such that an all-cube-face star polyhedron results.

Besides regular icosahedra experimental observations of the shape evolution with growth parameter mainly include examples that exhibit dimples of various size at the emergence points of twin junctions as is shown in Fig. 16 for boron suboxide particles [31], as well as twin boundary grooving of varying extent [27, 32]. Regular icosahedra can often be found in particle ensembles of transition metals [33] while icosahedra with dimples and grooves at the surface frequently occur for diamond and boron suboxide nanoparticles fabricated, for example, by chemical vapour deposition, acetylene flame synthesis, and high pressure melt synthesis, respectively [27, 31, 32]. Only one report has been given up to now on icosahedra having a starry shape where Burt et al. [34] propose a model of these gold particles obtained by solution growth which consists of trigonal pyramids capping the corresponding faces of a regular icosahedron. However, the additional assumption that these pyramids have tetrahedral shape and are bounded by [111] surfaces requires not only capping tetrahedra situated in twin relation with respect to their base tetrahedron, but it also excludes to consider this star-shaped polyhedron as being due to growth conditions favouring a cube face-bounded polyhedron. This will be discussed in more detail in the next section.

**Fig. 15.** Evolution of icosahedron morphology with growth parameter affecting the subunit shape: (a) octahedron; (b) truncated octahedron; (c) cuboctahedron; (d) cube.

**Fig. 16.** SEM images of boron suboxide icosahedral particles, adapted with permission from [31], which exhibit dimples of various size at the emergence points of twin junctions.

**4. Strongly anisotropic growth of multiply twinned particles**

**4.1 Branching growth**

Branching growth as directional crystallization along the apex directions of a polyhedral crystal is induced by concentration effects in a concentric diffusion field formed around the growing crystal [3]. Similar to the case of single crystalline particles various branched morphologies can be found in multiply twinned particles with and without including the twin boundaries. Silicon precipitates grown in Al–Si melt or fabricated by laser processing of corresponding alloy materials have been reported to exhibit a branched structure where the branches extend like fingers from the twin boundary corners and proceed straightaway with these boundaries [35, 36]. Such twin finger decahedra have been observed also for gold and platinum nanoparticles fabricated by solution synthesis [37–39]. As an example Fig. 17 shows a TEM image of a twin finger decahedron of gold [38] together with the schematic drawing of two model subunits containing indented trigonal faces surrounding a concave edge from which the configuration of the MTP may be imagined. The excessive growth along the twin boundaries is thought to result from unfavourable growth conditions at the periphery of tetrahedral subunits. Branching growth also is observed for single crystalline metal particles formed in the above mentioned solution routes of synthesis [37–39].

Another situation is met with the different geometry of star decahedra which already exhibit distinctly protruding apexes. Under certain conditions of growth star decahedra formed by chemical vapour deposition in boron nitride platelets [40, 41] may tend to develop a fivefold branched morphology as it has been observed for relatively high deposition temperature and relatively low total gas pressure [42]. Here the branching does not extend from the twin boundaries emergence points, but it proceeds from the star tips of the subunits, so as to replace the tips by finger-like protrusions. Quite accordingly, the spiky icosahedron mentioned above [34] could be understood in terms of branching growth starting at the tips of a star icosahedron. It may be recognized from the TEM image

**Fig. 17.** HREM image of a finger decahedron of gold from solution synthesis, adapted with permission from [38], (a) together with schematic drawing of two model subunits containing indented trigonal faces surrounding a concave edge (b) to be joined along a twin plane (arrowed) and to be completed accordingly by three matching subunits.
in Fig. 18 that the pyramids capping this icosahedral particle obviously appear more pointed than expected for segments of a cube capping the faces of a regular icosahedron as shown in Fig. 15d. Furthermore, from dark-field images presented in the Burt et al. article [34] it can be concluded that there is no twin boundary between the base tetrahedra forming the icosahedron and their respective capping pyramids. That means, the spikes making the particles appear like star polyhedra most probably result from a kind of branching growth that also is observed for single crystalline particles obtained in the same synthesis.

4.2 Unidirectional growth

One-dimensional nanostructures like nanorods or nanowires are mostly obtained by template-directed, surfactant-assisted, and/or seed-mediated processes that either confine the growth to one dimension or act as favourable sites for the adsorption of reactant molecules. Defect-mediated or twin-induced growth based on the effect of twin boundaries and fivefold twin junctions to enable reasonable growth rates at low precursor concentration [5, 43] may even allow promoter-free formation of such nanostructures. The elongation of multiply twinned particles by unidirectional growth proceeds via distinctly different processes for decahedra and icosahedra, respectively.

4.2.1 Elongated decahedral structures

Elongated decahedral structures simply may be achieved by axial growth of a prism decahedron along its fivefold twin junction, provided a distinct growth rate anisotropy or some kind of surface modification will prevent significant radial growth. The rod shape formed thereupon corresponds to a pentagonal prism with pentagonal pyramids at the rod tips. Pentagonal rods and needles of natural origin have been reported rather early for gold. The needle shown as an example of 1877 [44] in Fig. 19 carries some additional twin species of rhombic prism and trigonal bipyramid shape on the pentagonal prism stem. The needle tip obviously does not display five {111} faces as being expected for decahedral structures, but has a more spiky shape and faces corresponding to a half pentagonal trapezohedron. Two different growth modes are known for the directed growth of decahedra along their fivefold twin junction. One simply consists in an elongation of a decahedral particle having regular or modified shape as it is schematically drawn for the prism and the star decahedron in Fig. 20a and b. The other exhibits a modification of {100} and {111} prism faces to periodically stepped faces.
so as to result in oblong pentagonal bipyramid shapes as it is drawn in Fig. 20c and d.

Figure 21 illustrates outline and geometry of a boron suboxide nanowire that is supposed to result from a star decahedron by directed growth along the twin junction in a solid state reaction [45]. Although this image is not much convincing because of the rounded tips of the star-shaped cross-section, the multiple twinned structure is confirmed by selected area electron diffraction. The corresponding structural model in Fig. 21b features the atomic nature of the terminating surfaces and twin planes (arrowed). The boron suboxid structure (rhombohedral, space group 166) with a dihedral angle of 71.8° between two adjacent twin planes appears to be well suited for the creation of cyclic twinned configurations. Quite similar twinning, that means prisms with striking five-pointed, star-shaped cross section, has been observed in pentagonite, a natural calcium vanadium silicate mineral [46]. The special geometry of the pentagonite crystal structure (orthorhombic, space group 36) with a dihedral angle of 72.7° between two adjacent twin planes readily permits fivefold cyclic twinning. An example for pentagonal rods grown from a prism decahedron [11, 46–48] is shown in Fig. 22. The structural characterization by high resolution electron microscopy of the silver nanorods grown by inert-gas aggregation technique [11] makes use of their 36° rotational periodicity. Distinctly different image contrast appearance is obtained for rotating the rod by 18° from a base-orientation where the electron beam hits perpendicular to a prism face (see, for example, the hatched area in the schematic drawing, Fig. 22b) to a side-orientation where the electron beam runs parallel to a prism face.

At particles with decahedron shape anisotropic growth also may proceed, in addition to the preferred growth along the fivefold twin junction, by preferred growth along a reentrant edge at the outer bounds of one of the twin planes. Thus unidirectional radial growth is combined with axial growth so as to create plates of asymmetric structure as it is demonstrated in Fig. 23 by an example of gold from solution synthesis [49]. The twin boundary extended this way is marked by hatching in the schematic drawing of Fig. 23b. Another type of deviation from the pyramid capped pentagonal prism shape of multiply twinned rods is reported for copper rods grown by metal-organic chemical vapour deposition [50] where the radial prism edges uniformly increase during growth leading to a baseball bat-like shape. An opposite way of modification of decahedron-based multiply twinned rods consists in a uniform decrease of the radial prism edges during growth leading to an oblong pentagonal bipyramid shape as it has been reported for the Ag(+)-assisted solution synthesis of gold nanostructures [51–55]. Apparently, the {100} prism faces of pentagonal rods have been replaced by periodically stepped faces like {11n}. An example is given in Fig. 24 where the schematic representation points to a certain rounding effect at the tips of these particles. Even
more complicated structures have been observed very recently in the seed-mediated synthesis of gold nanocrystals which exhibit in addition to this oblong pentagonal bipyramid shape also a star-shaped cross-section [56] as schematically drawn in Fig. 20d. Likewise, molybdenum nanotrees have been formed in ambient air using atmospheric-pressure microplasma [57] where branching growth along the twin boundaries in combination with preferred growth along the twin junction produces a fivefold-twinned star-shaped cross-section with gaps between branches and twigs inclined upwards to the stem by about 30° which exhibit increasing extension from the base to the tip.

4.2.2 Elongated icosahedral structures

Icosahedron-based structures do not by far show as much tendency for anisotropic growth as it is observed for decahedral particles. One of the main reasons should be their minimal surface energy because of the only slight difference to a nearly spherical shape. Another one is the highly uniform configuration. From a central point shared by 20 tetrahedral subunits fivefold twin junctions extend in 12 directions around which 30 twin boundaries are grouped. Nevertheless, there are two exceptions which favour anisotropic growth variations also for icosahedra. One is given by a certain probability of uniaxial growth along one of the twin junctions as it is drawn schematically in Fig. 25. In principle this may be understood as a transition from an icosahedral to a decahedral structure and the resulting particle configuration is readily obtained by adding a pyramid-capped pentagonal rod to an incomplete icosahedron of 15 subunits consisting of a decahedron plus a pentagonal antiprism.

Such hybrid multiply twinned structures have been reported for gold and silver particles to result from coalescence processes [58], and for FePt particles owing to a lack in stability during the growth [59]. For the latter example Fig. 26 shows a HREM image together with an image contrast simulation according to a model sketched in Fig. 25. In both cases there is achieved only a limited extent of anisotropic growth. Another way to overcome the anisotropy restraint is the directed growth of icosahedral structures by preferred stacking of tetrahedral subunits along one fivefold twin junction that has been experimentally observed in metal particles grown on crystalline substrates via PVD [12, 16, 58]. As it may be deduced from the schematically drawing in Fig. 27 it needs a certain
growth configuration being in favour of attaching tetrahedral subunits so as to create pentagonal antiprisms and pentagonal bipyramids along one of the twin junctions present in an icosahedral particle. The resulting structure could be named double icosahedron or twin icosahedron. Appropriate growth configurations are met with straight surface steps of substrate crystals that provide preferred sites of accommodation of vapour species so as to promote growth and coalescence of particles along the step line. Figure 28a shows a HREM image of such a double icosahedron gold particle consisting of two icosahedra in twin position that share one common decahedron as sketched schematically in Fig. 28b [12]. From Fig. 27 one may recognize that the particle morphology corresponds to a pentagonal bi-antiprism pyramid-capped on both sides. Continuation of such template-directed growth should lead to rod-like particles as shown in Fig. 28c having multi-antiprism surface morphology.

5. Summary

An overview is given on the considerable number of weakly as well as strongly anisotropic forms of nanoparticle shape resulting from cyclic pseudo-fivefold twinning as constitutive building principle. Besides the shape variations due to growth stacking of tetrahedral subunits this overview includes the nearly regular polyhedron shape variations due to growth rate changes and the strongly anisotropic growth of multiply twinned particles occurring as branching growth, or as unidirectional growth, respectively. Generally, the weakly anisotropic shape evolution as well as the strongly anisotropic growth of decahedral particles appear more rich in variety as those of icosahedral particles. It is worthwhile to point out that for a certain class of materials multiple twinning represents a reasonable means to approach the issue of one-dimensional nanostructures.

Acknowledgments. The author would like to thank all colleagues close and far who made available to him results related to the subject of multiply twinned particles in the course of nearly three decades of consideration.

References


Fig. 28. HREM image of a double icosahedron gold particle (a) on crystalline substrate, adapted with permission from [12], consisting of two icosahedra in twin position which share one common decahedron as sketched schematically in (b). Continuation of this directed growth leads to rod-like particles with multi-antiprism morphology as shown in (c).


