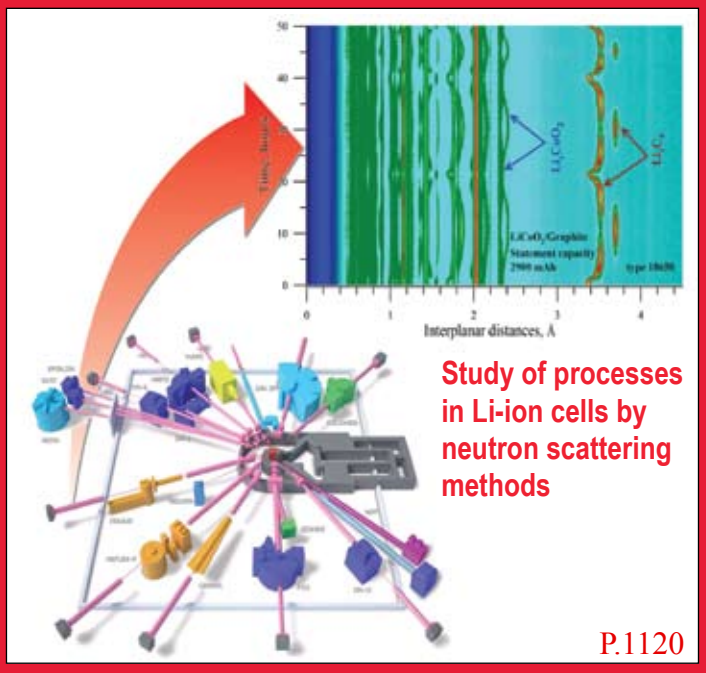
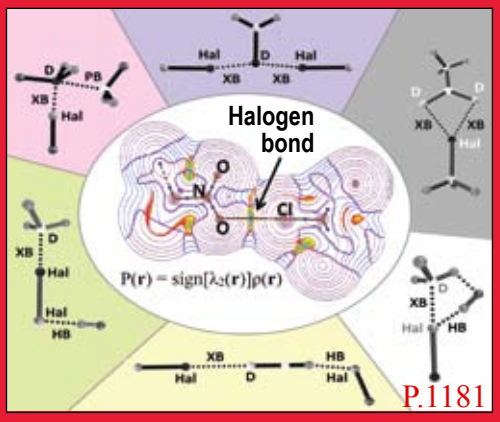
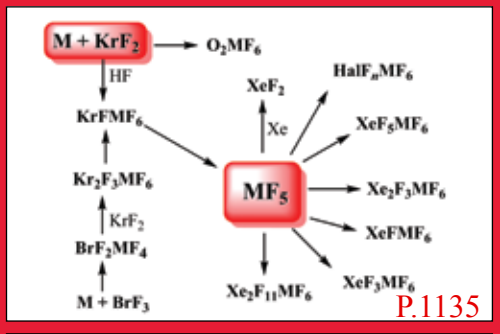
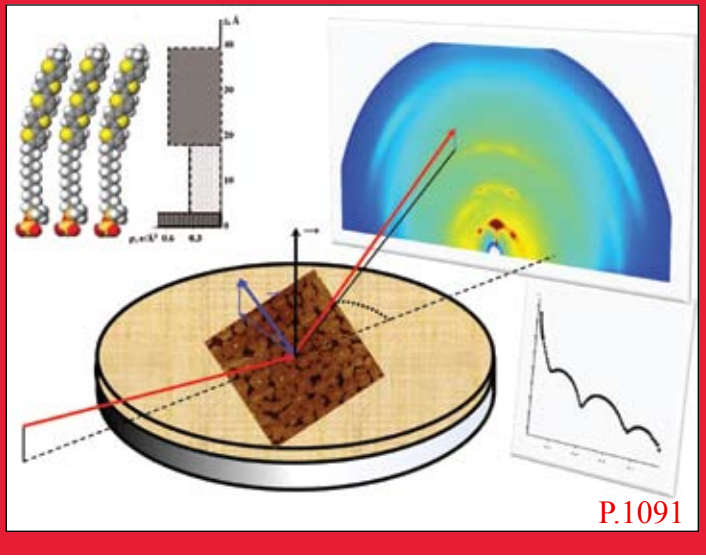
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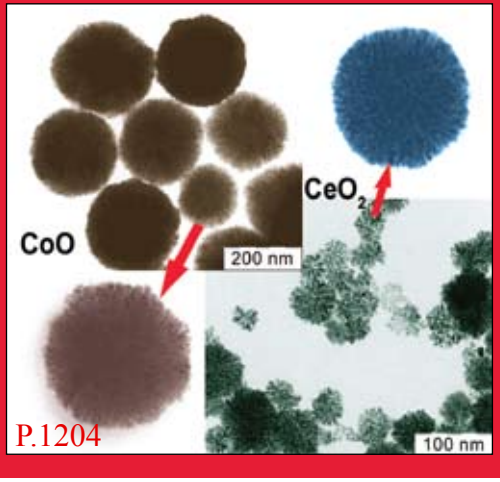
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Oriented attachment of particles: 100 years of investigations of non-classical crystal growth

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The results of investigations of non-classical crystal growth by the oriented attachment mechanism are summarized. The data published since the end of the 19th century are considered, the attention being focused on analysis of publications of the last 15 years. Data on characteristic features of the oriented attachment of particles are described systematically. The experimental methods used to elucidate the peculiarities of non-classical crystal growth, including *in situ* methods, are discussed. The prospects of application of the oriented attachment of particles for the formation of various materials are demonstrated.
The bibliography includes 227 references.

Contents

I. Introduction 1204
II. Brief description of the classical models of crystal nucleation and growth 1205
III. Crystal nucleation and growth according to the oriented attachment model 1205
IV. Conclusion 1219

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I. Introduction

Crystallization is one of the most important physicochemical processes. Crystal structure determines most of properties of substances in the condensed state; this is why the modern material science relies in great part on the achievements of crystallography and crystal chemistry.

Historically, the interest in crystallization was associated with making crystals more aesthetically pleasing. The fundamentals of the crystal growth process were established back in the late 18th century. Since then, abundant experimental material has been collected and the paradigm of the classical theory of crystal growth has been formulated: the growth of any crystal proceeds due to the attachment of new building units (atoms, ions, molecules, or their complexes) from the medium (solution, melt, vapour or solid) to the surface.[1]

The classical theory of crystallization including its version, the theory of lateral spiral growth developed in the studies of Burton, Cabrera and Frank,[2] has been used for many years to describe crystal growth processes including the development of industrial processes for manufacture of crystals. However, the relevant models operate only under limited conditions which are not always met in practice. In turn, the so-called non-classical models of crystallization[3] postulate that crystals can grow due to the

attachment of solid phase blocks rather than single atoms, ions or molecules to the growing surface. Note that both classical and non-classical crystallization mechanisms involve the common stage of formation of primary particles (nuclei) the further growth of which proceeds by different routes.

The interest in non-classical crystallization models was dramatically quickened in the past decade, which was due to the rapid development of two key areas of material science associated with the synthesis and investigation of nanomaterials and biomaterials. It is in these areas that scientists most often come across structures the formation of which cannot be explained based on traditional concepts. The development of non-classical crystallization models is very important as regards elaboration of new types of functional materials including composite nanomaterials, hybrid organic-inorganic materials, multilevel hierarchical materials, *etc*.[3] Note that the non-classical mechanisms of crystal growth are involved most often in the synthesis of solid-state materials by chemical reactions occurring in aqueous and non-aqueous media.

The present review generalizes the results of studies dealing with the phenomenon of oriented attachment of particles, which started in the late 19th century. Attention is focused on the analysis of recent studies published in the last 15 years.

II. Brief description of the classical models of crystal nucleation and growth

The thermodynamic description of homogeneous crystal nucleation is based on the Gibbs theory that takes into account the decrease in the system free energy upon nucleation of a new phase and the increase in the free energy due to the formation of a new interface. According to this theory, the new-phase particles can be thermodynamically stable only once they reach a certain critical size. As the system deviates from equilibrium (*e.g.*, due to supersaturation or overcooling of the melt), the potential barrier to new phase formation and the radius of the critical nucleus also decrease. In the presence of heterophase (*e.g.*, in the presence of an interface), the potential barrier also substantially lowers.[4–6]

The crystal growth is traditionally considered as a spontaneous process. The necessary condition for such process is deviation of the system from equilibrium, which results in redistribution of components between the growth medium and the growing crystal and, ultimately, in increase in the crystal size. Usually a transient adsorption layer is assumed to be present between the crystal and the growth medium. Having reached the surface, the molecules and ions of the growth substance interact with it while retaining considerable freedom as regards their migration over the surface. During crystal growth, the physicochemical transformations occur in the following sequence:

— diffusion of the growth substance from the solution bulk to the crystal;

— adsorption of the growth substance on the crystal surface;

— migration of the growth substance over the crystal surface;

— further building of the crystal lattice.

A lot of studies (*e.g.*, see Refs 1 and 7) present quantitative descriptions of the crystal growth within the framework of the Burton – Cabrera – Frank lateral spiral growth theory. In this theory, the key role is given to dislocations, which provide the presence of open growth steps on the crystal faces. In particular, this theory was substantiated by *in situ* atomic force microscopy examination of the migration of growth spirals.[8]

The evolution of crystals after depletion of the growth substance is determined by their shape and size distribution. According to the Gibbs – Thomson equation with the Tolman correction (l_0),

$$S = S_\infty \exp\left[\frac{2\sigma v_0}{kT}\left(\frac{V}{Q} + l_0\right)^{-1}\right] \quad (1)$$

the solubility of a crystal of a given size (S) increases with the increase in its surface area (Q) to volume (V) ratio (*i.e.*, with decrease in the crystal size).† This is why in an assembly of polydisperse particles, finer particles are eventually absorbed by coarser particles [through their common environment (solution), the particles can exchange the substance].[9] This phenomenon is called the isothermal distillation or the Ostwald ripening. Note that the Ostwald ripening mechanism, which relies on the thermodynamic concept that the particle solubility is size-dependent, is not directly related to any particular model of particle growth mechanism including the spiral lateral model.

III. Crystal nucleation and growth according to the oriented attachment model

III.1. General information on the mechanism of oriented attachment of particles

The classical theory of crystallization adequately describes the growth of crystals of poorly soluble substances (calcium carbonate or oxalate, *etc*.) from dilute solutions but stops to be valid at high degrees of supersaturation. From the standpoint of this theory, it is difficult to explain the formation of single-crystalline micro- and nanoparticles with untypical habitus under certain conditions, for instance, quasi-one-dimensional nanorods of di- and trivalent iron oxides,[10] cerium dioxide [11] and barium fluoride [12] and also barium sulfate single crystals with 10-fold axial symmetry.[3, 13] Finally, it is known that biomineralization may produce single crystals of very complicated shapes (for example, calcite crystals in foraminifera shells),[14] which formally contradicts the Curie – Gibbs – Wulff principle.

This and other examples which can be found in numerous publications indicate that crystal formation can occur not only according to the simplest model of nucleation and subsequent growth of solid-phase particles through dissolution of the substance in the growth medium but also according to a more intricate mechanism, namely, as a result of oriented attachment of particles. According to this mechanism, supersaturation can be initially eliminated due to formation of primary nanoparticles, which later aggregate, are ordered and merge together to give coarser single-crystalline particles. In other words, nanoparticles perform the same mass-transfer function at the mesoscopic level as is accomplished by ions, molecules or atoms at the

† Other quantities present in Eqn (1): S_∞ is the macrocrystal solubility, σ if the surface tension, v_0 is the molecular volume, k is the Boltzmann constant and T is temperature.

microlevel, the crystal growth occuring from heterogeneous (colloid) solutions rather than from homogeneous (true) solutions. It should be noted that in terms of the non-classical model, the stages of nucleation and growth of particles are apparently inseparable.[15] In contrast to the Ostwald ripening, this model adequately describes the processes of particle growth under the conditions far from thermodynamic equilibrium, which are most often realized in practice during the synthesis of nanosized materials.

III.2. History of the discovery of the phenomenon of oriented attachment of particles

The idea that crystals can grow according to the mechanism of oriented attachment of particles (the mechanism of microblock growth) was put forward by crystallographers back at the turn of 18th and 19th centuries.[16] They assumed that mineral crystals can form due to the in-parallel attachment of numerous fine subspecies enveloped by common faces.

Gaubert[17] has shown that slow evaporation of water from a lead nitrate solution affords single crystals of octahedral habitus. Stirring the solution already containing lead nitrate crystals resulted in their attachment to form spinel-type twins. In the subsequent experiments, Gaubert stained some of lead nitrate crystals with Methylene Blue and placed them into a saturated solution containing similar uncoloured crystals. He observed the formation of bicoloured crystals, both twinned and consisting of individual crystals grown together in the parallel orientation. Based on his observations, Gaubert formulated the thesis on the possibility of regular attachment of independently grown crystals that occasionally come into contact with one another during the growth.

In his paper 'The Crystallization Process', Fedorov[18] has noted that under certain conditions, entire plates of strictly parallel particles can quickly form during crystallization; the plates, which immediately cover the whole face of the crystal or its greater part, consist of numerous layers of particles rather than a single layer. Shubnikov and Schaskolsky[19,20] have found that fine potassium alum crystals can aggregate with coarse cubic crystals of the same substance to be arranged preferentially in parallel to one another, partly in the twinning position and only sometimes along the common edge or not in the strictly parallel position. Based on these experiments, Shubnikov[19] put forward the model of crystal formation through attachment of the so-called submicron-sized particles (Fig. 1).

In his review, Sheftal[21] described several experiments supporting the mechanism of oriented attachment of particles. Particularly, in an experiment which partly resembled that described above, he observed how fine quartz crystals got attached in parallel arrangement to a seed crystal. The more so, later, the neighbouring crystals grew together to form a common face due to the similar orientation. Experiments on the gas-phase growth of thin films have demonstrated that silicon crystals of $\sim$30 nm size are attached together to form well faceted and outwardly homogeneous crystals of 150–200 μm size. It is interesting that according to Sheftal, even at low degrees of supersaturation, the crystal lattice is not apparently built of solely individual atoms and molecules.[21]

The key contribution to development of the theory of nucleation and crystal growth by the oriented attachment mechanism was made by Yushkin. In his monograph,[16] he considered the specific features of crystal growth from the standpoint of colloid chemistry, particularly, he analyzed how the shape of particles affects their capability for oriented attachment. He pointed out that the electric double layer, which prevents coalescence of particles in solution, shields only the flat faces of crystalline particles being absent on sharp vertices and edges; hence, the state of the system in the latter sites is close to the isoelectric state and, moreover, there are more dangling bonds there. As the particles approach one another by their faces, a potential energy barrier arises between them which stimulates repulsion of particles (for elemental sulfur this barrier was assessed to be 8–12 kJ mol^{-1}). When particles approach one another by vertices or edges, they can stick together. The presence of a maximum in the curve describing the interaction energy of approaching particles *vs*. the distance between them means that the rate of mutual approach decreases at close distances. Due to this retardation, the particles have enough time to be oriented in parallel to one another rather than aggregate chaotically. The latter assumption was confirmed by experimental data illustrating how sulfur particles aggregate in natural colloid solutions (Fig. 2).[16] Note that according to semiquantitative estimates carried out in relation to the attachment of calcite particles,[22] the degree of relative orientation of crystals in aggregates was the highest at the low ionic strength of the medium.

It was noted[16] that the mechanism of crystal growth from colloid solutions is by and large analogous to the



Figure 1. Illustration of attachment of submicron particles according to the Shubnikov scheme.[19]

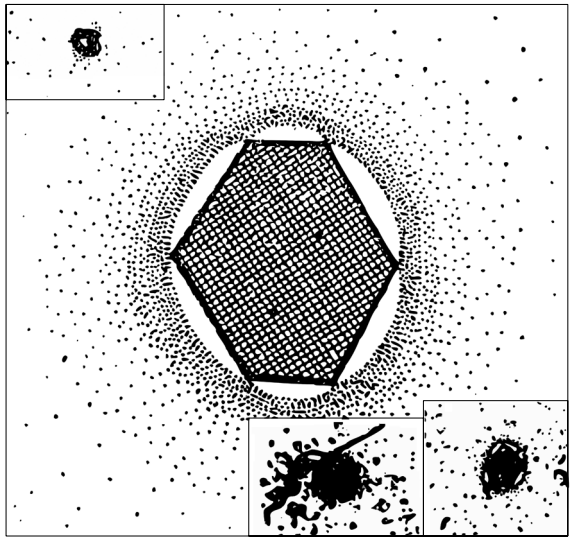


Figure 2. Illustration of the ways of agglomeration of sulfur microparticles in a natural colloid solution.[16]
The inserts show examples of particle agglomeration.



Figure 3. Ways of assembling of crystal-forming particles in the long-range action zone of a growing crystal.[16]

mechanism of attachment of particles described above. It is interesting that in natural colloid solutions of sulfur, a sort of clouds of colloid particles can be observed around large crystals, being in contact with the crystals by their vertices and edges (Fig. 3). The thickness of the colloid particle layer varies from 100 μm to 1 mm. Further building of the crystal lattice due to addition of colloid particles proceeds in the flat layers that propagate from the generation sites on the vertices and edges of the crystal towards the centre of faces. The unequal size, irregular shape and mutual orientations of building blocks associated with the high rate of this process give rise to numerous defects in the growing crystals which, however, can be eliminated as a result of diffusion. The maximum size of particles capable of orientation in parallel to one another can reach ~1 mm as evidenced by numerous observations.[16]

The shape of crystals formed by the oriented attachment mechanism is very sensitive to the composition of the medium. The most significant effect is due to the chemical composition and pH of solution, a less pronounced effect is exerted by temperature, and pressure influences to the least extent.[16] It should be noted that crystals grown from colloid rather than true solutions are more susceptible to gravitational deformations of their shape.

Based on analysis of a considerable body of experimental results, the following distinguishing features of crystals formed by the oriented attachment mechanism have been formulated:[16]

— the high degree of patchiness of the crystal at the micro- and macrolevel;

— the enhanced porosity and the low density as compared with theoretical values;

— the low dielectric permittivity;

— plenty of mother solution inclusions (see also Ref. 23);

— the large thickness of elementary growth layers;

— the trend towards formation of skeleton crystals and parallel aggregates;

— gravitational deformation of the crystals.

This list of characteristic features (with some obvious exceptions) can be used to elucidate the most probable mechanism of formation for biomaterials and nanomaterials.

Buyanov and Krivoruchko[24,25] have developed the crystallization theory for poorly soluble substances (first of all, transition metal hydroxo compounds) by the 'oriented addition mechanism'. According to this theory, the gels of hydroxo compounds of metals deposited from salt solutions consist of isotropic primary particles incapable of specific orientation interactions with one another. During ageing of the gels, the primary particles are restructured, which is accompanied by the appearance of completely or partly crystallized particles. The completely crystallized particles, which were called the crystallization centres, have properties resembing the properties of single crystals and cannot interact with one another. The primary particles still occurring in the state far from the state of crystallization centres were called the nuclei. The nuclei have almost completely formed faces and, hence, they can undergo oriented interaction with crystallization centres and, due to residual lability of their structure, they can be attached to the corresponding faces of crystallization centres. Thus, the nuclei serve as building blocks for the formation of coarser items, which are called secondary crystals. In the planes of attachment of the nuclei to the crystallization centres or to the secondary crystals, there remain defects, as has been confirmed experimentally.[24] Thus the secondary crystals have a block structure. A study of the thermal stability of secondary crystals demonstrated[25] that their destruction occurs first of all along the planes of block attachment.

In the mid-1960s, Suito and Uyeda[26] put forward the hypothesis on the possibility of the so-called mosaic growth of crystals. In a study of gold[27] and silver[28] sols by transmission electron microscopy (TEM), they have found that most of colloid particles contain various twinning defects formed due to the interaction of primary nuclei (for instance, the size of such gold nuclei was 1 – 2 nm). They have observed[26] that the surface of flat gold crystals during their growth contained numerous protrusions with hexagonal profiles; however, the surface was completely smoothed out after the completion of crystal growth. Based on these data, they assumed that the growth proceeds by the attachment of colloid particles with sizes below several nm to the surface of the growing crystal; in the case of considerable misorientation of particles, screw dislocations are formed which provide the further growth of particles. It is interesting that in supersaturated solutions, the rate of single crystal growth substantially increases (by a factor of 2 – 5) in the presence of microcrystals of the same substance.[29,30] This is probably due to the fact that attachment of a microcrystal to a single crystal is accompanied by the formation of steps on the single crystal surface.[30]

Abundant experimental evidence for the possible growth of crystals *via* attachment of primary particles was obtained in the research aimed at the development of photographic materials, particularly, flat crystals of silver halides (see also Section III.4). Thus, Larichev *et al.*[31 – 35] directly postulated the existence of two growth mechanisms for silver halides: ionic and coalescence ones; they stressed the key role of the Coulomb interaction, which leads exactly to oriented coalescence. They have shown that the coalescence growth mechanism becomes predominant with a decrease in the substance solubility; moreover, the stage of coalescence

growth of silver halide crystals is usually followed by the stage of their recrystallization by the ionic mechanism.[36]

Analogous hypotheses were also stated abroad.[37–39] Particularly, according to the definition given by Antoniades and Wey,[39] coalescence is a phenomenon in which two (and more) crystalline particles are united to form a new coarser particle; the growth of particles by the coalescence mechanism includes the stages of flocculation (formation of loose aggregates) and coalescence as such. According to different authors, the distinguishing features of this mechanism that point to the absence of any considerable contribution of diffusion transfer are as follows:

— the absence of any dependence of the thickness of flat crystals on their diameter;

— invariance of the thickness of flat crystals during their growth;

— the gradual disappearance of primary fine crystals, their size invariable.

Several studies of paramount importance for the development of the non-classical theory of crystallization in liquid and gas media were carried out under supervision of Melikhov.[40–42] The formation of anisotropic filament crystals upon aggregation of isotropic crystals was experimentally demonstrated for the first time in Ref. 40. There, the possibility of the two-stage oriented attachment process (primary particles → primary aggregate, primary aggregates → secondary aggregate)[41] was stated and the formation of aggregates of disordered particles which could later dissociate or be restructured to afford regular bodies was hypothesized.[42] The crystals formed as a result of oriented attachment were proposed to be called pseudo-single crystals and the phenomenon of their formation was called the single-crystal mimicry.[42]

Additional data on the existence of non-classical crystallization mechanisms were obtained in a study of epitaxial growth processes by the Volmer–Weber mechanism.[43,44] In the latter case, the mutual orientation of the attached microcrystals depends on the crystalline support. Distler *et al.*[45,46] obtained a huge body of information on orientation and reorientation of single crystals on the surface of various supports during the growth of thin films. It was noted[47,48] that in some cases, the presence of intermediate amorphous layers of polar dielectrics including water between the microscrystal and the anisotropic surface makes the effect of crystal orientation still more pronounced. This suggests that the orientational action of van der Waals forces can propagate to a considerable distance even through amorphous layers. It should be noted that the mobility of crystals on an anisotropic surface is very high and crystal reorientation occurs at a high rate.

Based on analysis of experimental data and theoretical considerations, it was stated that crystalline particles located on an anisotropic surface can undergo a sort of orientational phase transition. According to the model of this transition,[48] the fraction of oriented single crystals depends on their linear size by the following relationship:

$$\frac{n}{n_0} \propto \frac{L}{L_c}, \qquad (2)$$

where n is the number of reoriented microcrystals, n_0 is the total number of microcrystals, L is the microcrystal perimeter, L_c is the critical value of L which, once reached, means

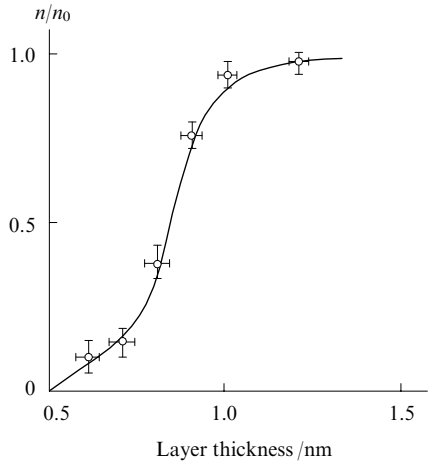


Figure 4. Relative fraction of oriented AgCl microcrystals on the surface of a negative thioglycine sulfate domain *vs.* average thickness of the AgCl layer.[48]

reorientation of virtually all microcrystals. This dependence agrees well with experimental data (Fig. 4).

In conclusion, we would like to note that the concept of non-classical crystal growth and also some experimental facts substantiating this theory were discussed also in other numerous publications (*e.g.*, see Refs 49–54).

Unfortunately, the studies in the field of non-classical mechanism of crystal formation carried out in Russia were unnoticed abroad. This and also the considerable progress in the field of electron microscopy can explain the fact that in the late 1990s, Penn and Banfield[55–58] (University of California, Berkeley, USA) published a cycle of studies in which the phenomenon of oriented attachment of crystals was in fact rediscovered *de novo*.

The high-resolution TEM analysis of nanocrystalline titanium dioxide samples synthesized by the hydrothermal treatment of TiO_2 sols in deionized water at 100–250 °C for 1–255 h has demonstrated[55] that the original TiO_2 nanoparticles without any crystal structure defects are capable of oriented attachment. The attachment may be totally coherent or may give twinning defects (Fig. 5), *i.e.*, possible nuclei of the new phase. Later,[56] the sequence of stages giving rise to chains of aggegated anatase nanoparticles was demonstrated (Fig. 6). It deserves mention that Penn and Banfield[55–58] often observed the particle attachment by not only their edges but also their faces. Taking into account the fact that oriented attachment of TiO_2 nanoparticles at different pH proceeded at different frequencies, it was assumed that the attachment of particles occurs most likely in the vicinity of the isoelectric point. Upon the addition of acetic or adipic acid to colloid solutions of TiO_2, the probability of oriented attachment of particles decreased, apparently, because the nanoparticle surface was blocked by the molecules of these acids.[56] Later, additional studies demonstrated that the rate of particle growth by the oriented attachment mechanism substantially depends also on other factors determining the aggregative stability of disperse systems, in particular, on the solution ionic strength[59] (see also Ref. 22). At the same time, after the addition of an inert electrolyte, the measured rate constants for nanoparticle attachment turned out to be much lower as

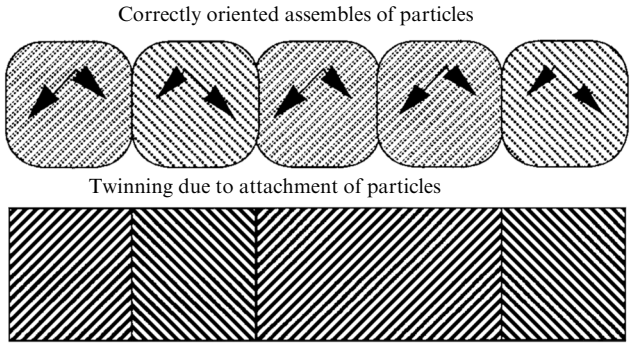


Figure 5. Illustration of oriented attachment of particles to afford twinning defects.[55]

compared with those calculated based on the Deryagin – Landau – Ferway – Overbeck equation.[60, 61]

Penn and Banfield[56, 57] also demonstrated that frequently encountered twinning defects in nanoparticles may be due to the fact that oriented attachment of particles requires that they be structurally compatible only in the plane of attachment. In turn, partial misorientation of crystallites upon attachment (Fig. 7 *a*) may lead to the formation of edge (Fig. 7 *b*), screw and mixed dislocations, because in the general case, the nanoparticle surface is not atomically smooth but contains steps of growth. The model of formation of nanoparticles containing continuous defects of different kinds was also described in detail.[57]

On the whole, the presence of twinning defects can be regarded as an additional distinctive feature of crystals

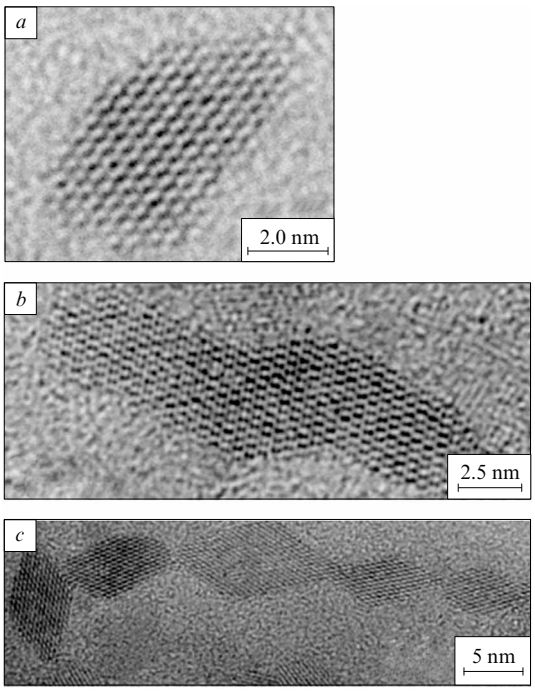


Figure 6. Formation of chains of attached anatase nanoparticles.[56]
(*a*) Primary TiO_2 crystal; (*b*) four primary crystals that form a single crystal by the oriented attachment mechanism; (*c*) five primary crystals connected by vertices.

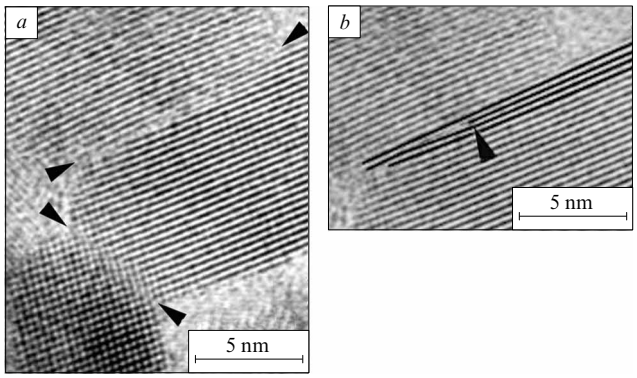


Figure 7. TEM images of three connected TiO_2 nanoparticles (*a*) and edge dislocation (*b*).[57]
Arrows show the boundaries of primary particles.

grown by the mechanism of oriented attachment. The detailed analysis of the corresponding experimental data can be found in a review.[62]

To summarize the foregoing, we can state that the whole body of studies[16 – 62] carried out in the 19th and 20th centuries reliably suggest that crystals can grow from colloid solutions by oriented attachment of particles. In the past decade, the interest of researchers in this subject considerably quickened. The number of relevant studies constantly increases and to date exceeds 1000, according to the Web of Science. Below we briefly survey the results concerning the oriented attachment of nanoparticles obtained in the period from 2000 to 2013.

III.3. Key methods used to analyze the oriented attachment of nanoparticles

Elucidation of the predominant mechanism of nanoparticle growth is still a challenge. In the past, the lack of physical methods suitable for studying nanomaterials was the main hindrance for elucidation of the mechanism of oriented attachment. At present, transmission electron microscopy and its high-resolution version (HR TEM) are used, most often, to study the mechanism of nanoparticle growth. Other methods for determination of the average size of nanoparticles or their size distribution are also used in certain cases (albeit not too often). Below we consider the advantages and drawbacks of these methods.

It should be emphasized that the most reliable and comprehensive approach to elucidating the mechanism of crystal growth is the use of several complementary instrumental methods and comparison of the results. Unfortunately, this approach has been used very rarely (*e.g.*, see Refs 63, 64).

Transmission electron microscopy is the only direct method that allows one to visualize the oriented attachment of particles and, in particular, find particles with the habitus untypical of a given crystal structure, projections and pits on the surface and also various defects (including dislocations and twinning defects) that have appeared as a result of attachment.

The main drawback of TEM is its local character; considerable number of experiments ought to be carried out on different areas of the analyzed sample in order to retrieve statistically reliable information on the growth mechanism of nanoparticles. Moreover, the deposition of

the sample on a support and its subsequent high-vacuum electron-beam treatment may affect the microstructure of the sample, giving rise to some artifacts.

In recent years, the TEM studies of the nanoparticle growth have increasingly used special expedients. In particular, the mechanism of crystallization of silicalite-1 was studied by means of the cryogenic HR TEM.[65] It was shown that crystallization of this zeolite involves several stages and its crystals grow exactly *via* attachment of primary particles.

Using the *in situ* HR TEM, it has been shown[66] that merging of gold nanowires with the diameter of 3–10 nm can occur even at room temperature and at moderate pressure (~4.7 MPa). Such 'cold welding' proceeds most efficiently for nanowires of the same crystallographic orientation, especially, for two fragments of a broken wire. In this case, the attachment occurs at a sufficiently high rate and is completed in several minutes; moreover, the strength in the attachment site does not differ from the strength of the whole wires.

The use of modern liquid cells for HR TEM makes it possible to directly observe the nanoparticle growth in the liquid phase. Some of relevant examples are shown below (see Section III.5).

The advanced methods for analyzing the structure of particles formed upon orientational attachment include the high-resolution electron tomography. This method was used for the first time in *ex situ* studies of oriented attachment of cerium dioxide nanoparticles.[67] Under hydrothermal conditions, CeO_2 nanoparticles were formed that contained pores and channels with the diameter of 1–2 nm arranged along the crystallographic direction [110] and retained even after heating to 500 °C. Similar open and closed pores were also observed in α-Fe_2O_3 nanopartiles formed under hydrothermal conditions.[68–70] Tan *et al.*[67] assumed that the regular arranged pores may also form in other materials produced by the oriented attachment mechanism.

X-ray diffraction remains one of the most popular and efficient methods for analyzing nanomaterials. There are several approaches that make it possible to determine the average size[71,72] and size distribution[73] of nanoparticles based on diffraction data. In certain cases, the use of the relevant data in the kinetic analysis makes it possible to speculate on the predominant mechanism of nanoparticle growth (*e.g.*, see Ref. 74). For instance, to determine the growth mechanism for AlOOH nanoparticles at different pH values, the calculated and experimental diffraction patterns were compared[75] and it was concluded that oriented attachment of boehmite nanoparticles along the [100] direction induces specific changes in the relative intensities of diffraction peaks. Such an approach can also be used for other nanomaterials.

To determine the size and the relative orientation of crystallites (in particular, at different depth) in thin-film materials, one can use grazing incidence X-ray diffraction.[76] The corresponding time-resolved experiments can be implemented with the use of synchrotron sources of X-ray radiation.

Small-angle neutron scattering (SANS) and X-ray scattering techniques are widely used for acquiring structural information in the range of 1–100 nm (for ultrasmall-angle scattering, up to several micrometres). The analysis of scattering patterns provides information on the structure parameters such as the particle shape, size distribution and specific surface area. Such a large body of information provided by both methods makes them suitable for determination of the mechanism and kinetics of nanoparticle growth both *ex situ* and *in situ*.

The year 2006 marks the appearance of the first publication[77] devoted to the use of SANS in analyzing oriented attachment of nanoparticles. A study of the formation of silicalite-1 has shown that nanoparticles (~3 nm) formed upon the hydrolysis of tetraethyl orthosilicate in the presence of ethanol and water grow at a very low rate (~0.2 nm per day) for a sufficiently long time (half a year and longer). Then, at a certain instant, much coarser crystallites (with the size of up to several tens of nanometres) that grow much faster appear in the system (Fig. 8).

The abrupt change in the size of particles could not be explained in terms of the Ostwald ripening model. Based on the combined analysis of SANS and HR TEM data, it was shown[77] that the particles grow by the oriented attachment mechanism. It is noteworthy that a similar temporal evolution of the dependences of the SANS intensity on the transmitted pulse was observed by other authors[78] in their study devoted to coagulation of TiO_2 sol in the presence of KCl.

A SANS study of D,L-alanine crystallization has shown[79] that in the course of transformation of mesocrystals of this compound into true crystals, scattering typical of porous solids is replaced by scattering typical of dense monolithic solids. However, the SANS data given in the publication as such[79] are insufficient to substantiate the non-classical mechanism of crystallization.

It was shown[63] that SANS data can be used for revealing the particle growth by the oriented attachment mechanism without invoking any other auxillary methods. Thus, in a study of the growth of CeO_2 nanoparticles by reconstructing the particle size distribution functions based on the SANS data, it was shown that CeO_2 powders subjected to hydrothermal microwave treatment at 120–210 °C for 0.25–3h were characterized by a bimodal particle size distribution in which the position of the second peak approximately corresponded to twice the size of first-peak particles. As the temperature rose and the time of treatment increased, the position of peaks remained unchanged but their relative contributions changed (Fig. 9). The mentioned changes in the CeO_2 morphology cannot be explained in terms of the Ostwald ripening model. Indeed, when the particles grow according to this mechanism, the maximum

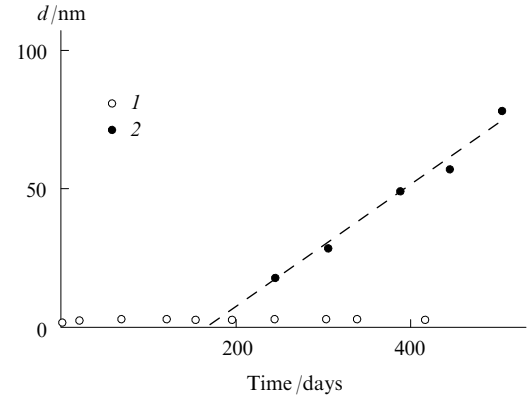


Figure 8. Dynamics of size variation for primary (*1*) and secondary (*2*) silicalite-1 particles according to SANS data.[77]

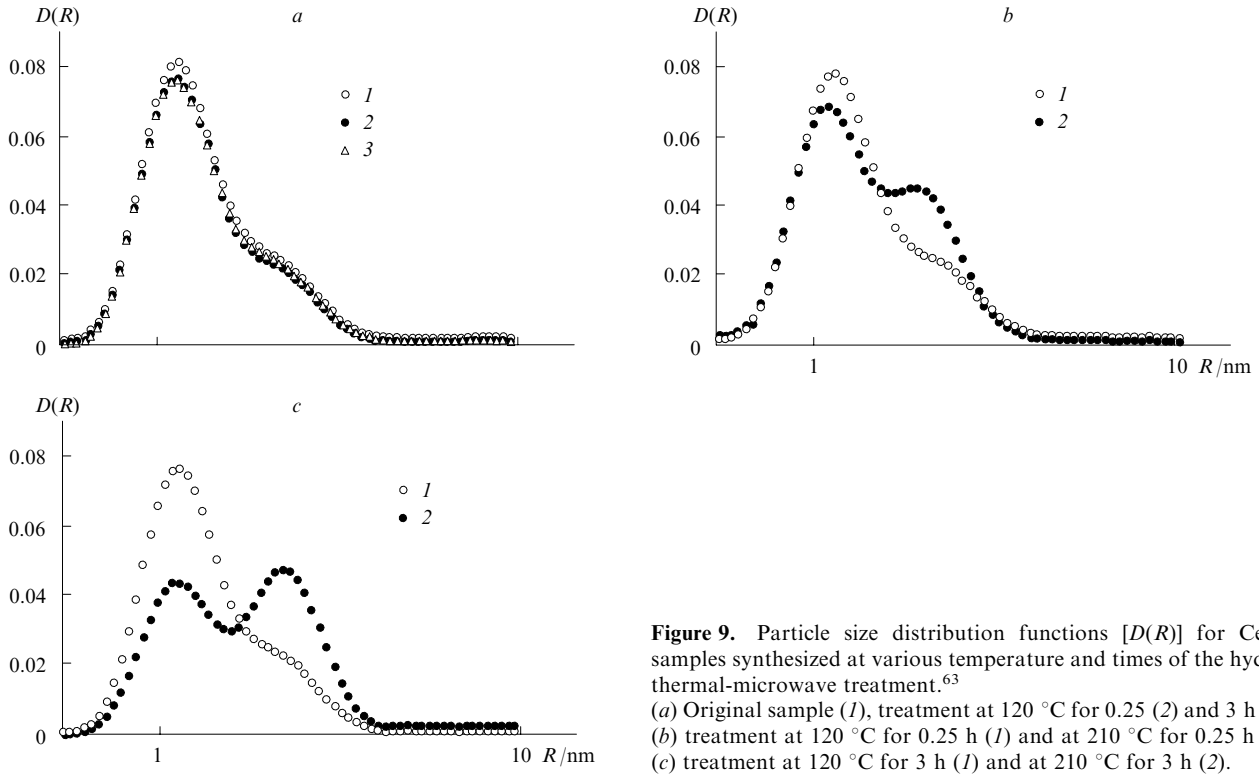


Figure 9. Particle size distribution functions [$D(R)$] for CeO_2 samples synthesized at various temperature and times of the hydrothermal-microwave treatment.[63]
(*a*) Original sample (*1*), treatment at 120 °C for 0.25 (*2*) and 3 h (*3*); (*b*) treatment at 120 °C for 0.25 h (*1*) and at 210 °C for 0.25 h (*2*); (*c*) treatment at 120 °C for 3 h (*1*) and at 210 °C for 3 h (*2*).

in the distribution curve should gradually shift towards larger sizes but this was not the case. At the same time, the changes in the particle size distribution curves were in good agreement with the growth model by the oriented attachment mechanism.

Later, the same conclusion concerning the bimodal size distribution of particles as a characteristic feature of the oriented attachment mechanism was drawn based on TEM data.[80,81]

Dynamic light scattering (DLS) is widely used in studying colloid solutions that contain particles measuring from 1 nm to several micrometres. The DLS studies of oriented attachment processes are usually based on the analysis of dynamics of changes in the nanoparticle size distribution during the synthesis; moreover, the chief merit of DLS is the possibility of *in situ* measurements. It was shown[81–83] that oriented attachment of nanoparticles is often accompanied by the formation of a bimodal size distribution of nanoparticles. At the same time, it should be noted that the bi- or polymodal distribution alone does not prove the oriented attachment, because similar result can be produced by usual aggregation of particles in solution. This is why for analysis of nanoparticle growth processes (*e.g.*, quasi-one-dimensional), it was proposed[64] to use a combination of the dynamic light scattering and the depolarized dynamic light scattering, which provides information on particle shape.

III.4. Synthesis of materials with the use of oriented attachment of nanoparticles

A key trend in modern studies in the field of non-classical mechanisms of nanoparticle growth is switching from mostly descriptive studies to the control over the particle growth aimed at the targeted design of advanced functional materials. At present, the oriented attachment of nanoparticles is used in the targeted synthesis of materials of all morphological types including one, two and three-dimensional materials.[84–86]

Water served as the growth medium in the majority of experiments devoted to the use of oriented attachment to synthesize nanostructures (*e.g.*, see Refs 87–90); however, synthesis can also be carried out in non-aqueous media, including solvothermal conditions.[91–93]

One and quasi-one-dimensional nanostructures. The synthesis of one-dimensional structures *via* oriented attachment has been described most thoroughly. According to the results of simulations,[94,95] one-dimensional structures are formed because under certain conditions, sticking of nanoparticles to the ends of growing one-dimensional crystals is energetically most favourable.

Methods have been proposed for the synthesis of various semiconducting materials including germanium nanorods,[96] nanorods and nanowires of metal chalcogenides (Bi_2Te_3,[97] CdS,[98] CdSe,[99] PbSe,[100] Ag_2Se,[101] CdTe,[102] *etc.*). Methods have also been developed for synthesizing metal nanorods and nanowires including those based on individual metals,[103] alloys[104–106] and intermetallic compounds.[107] The syntheses of nanorods and nanowires of metal oxides (Sb_2O_3,[108] ZnO,[109] SnO_2,[110,111] CeO_2,[112] Fe_2O_3[113]) and chains of merged α-Fe_2O_3 crystals (Fig. 10) are described. It was shown that oriented attachment can be used in preparing one-dimensional structures of the complex composition, *e.g.*, such as $BiVO_4$,[115] $LaMnO_{5+\delta}$,[116] $BaTiO_3$,[117] *etc.*

One-dimensional structures formed by the oriented attachment mechanism can additionally minimize the excessive surface energy due to their deformation. Thus, at the hydrothermal synthesis of titanium dioxide, the formation of curved nanorods was observed.[118] Similar distorted Ag_2Te nanorods were prepared with the use of the hydrothermal-microwave technique.[119]

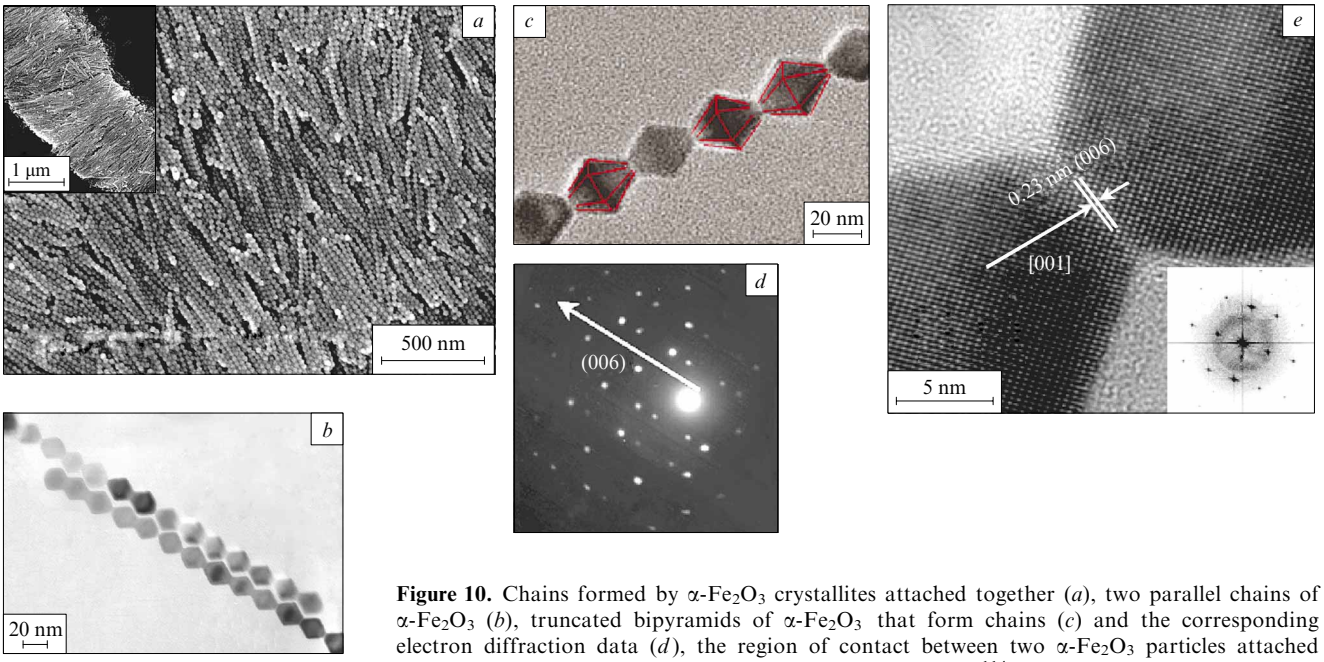


Figure 10. Chains formed by α-Fe_2O_3 crystallites attached together (*a*), two parallel chains of α-Fe_2O_3 (*b*), truncated bipyramids of α-Fe_2O_3 that form chains (*c*) and the corresponding electron diffraction data (*d*), the region of contact between two α-Fe_2O_3 particles attached together and the corresponding electron diffraction data (*e*).[114]

Under certain conditions, due to the oriented attachment of nanorods and nanowires, the more intricately organized structures can form, for instance, nanorings.[120–123] The detailed analysis of one of the possible mechanisms of formation of such objects has been reported.[124]

Finally, one-dimensional nanostructures can form also as a result of attachment of misoriented nanoparticles. Particularly, such a phenomenon was observed in the growth of gadolinium-doped cerium dioxide nanorods under supercritical conditions.[125]

Two-dimensional and quasi-two-dimensional nanostructures. The problem of performing oriented attachment to afford two-dimensional nanostructures is more complicated experimentally (and more rarely encountered in practice). The synthesis of 2D materials often involves the use of surfactants or ligands that are specifically sorbed on certain faces of growing crystals. Thus ultrathin sheets and nanoplates of CeO_2 (Fig. 11), PbS,[127] Ag,[128] Au,[129] SnSe,[130] ZnSe,[131] Bi_2S_3,[132] $V_2O_5 \cdot 1.6\,H_2O$,[133] α-Fe_2O_3,[134] Bi_2S_3 nanofabrics,[135] *etc*. were synthesized.

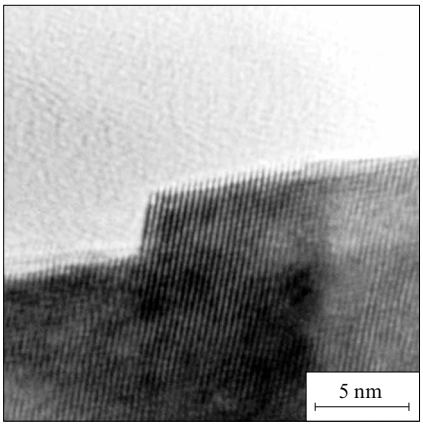


Figure 11. Microimage of a cerium dioxide nanoplate.[126]

It deserves mention that the formation of flat anisotropic microcrystals (with the thickness of 10–30 nm and the anisotropy ratio reaching 500 : 1) is well known for silver halides with highly symmetric lattice.[136] The interest in anisotropic microcrystals considerably increased after the Kodak company started to use them in the early 1980s for the production of photographic materials. The formation of flat crystals was attributed to the presence of twinning defects,[137] because the accelerated growth of crystals in the direction of twinning planes is associated with the fact that the latter crop out at the surface as dihedral reentrant grooves and the deposition of ions proceeds more easily on such surfaces than on crystal faces. On the other hand, according to Antoniades and Wey,[37] the formation of such twinned crystals is due to coalescence of microcrystal nuclei which usually leads to the {111} faceting. Note that the presence of the block (mosaic) structure for AgBr crystals was observed experimentally back in the 1950s–1960s by Herz *et al*.,[138, 139] who have shown that the misorientation angle between blocks is about several minutes.

In the recent years, other models were proposed to describe the mechanism of formation of anisotropic 2D nanostructures as a result of oriented attachment of particles. Thus, it was shown[140] that depending on synthetic conditions, the oriented attachment of nanocrystals can afford both cubic and plate crystals of FeS_2 (Fig. 12).

The change in the shape of FeS_2 single crystals (from cubic to plate-like) observed with the increase in the synthesis temperature is probably due to the fact that the primary FeS_2 crystals formed at relatively high temperatures are faceted preferentially by {110} planes, whereas at low temperatures, coarser crystals are formed that are faceted by {100} planes and characterized by much lower specific free surface energy. The difference in faceting determines the different character of both the aggegation and the subsequent attachment of crystals.

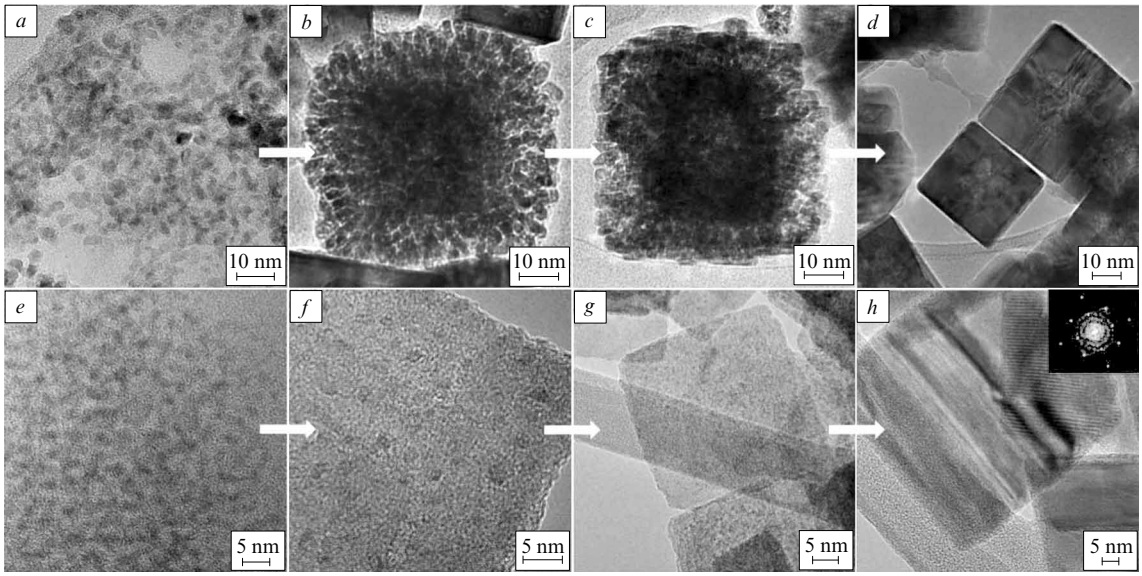


Figure 12. TEM images reflecting the sequence of stages in the oriented attachment of nanocrystals.[140]
(*a*) Original FeS_2 crystals, (*b*) agglomeration of crystallites, (*c*) attachment of crystallites, (*d*) recrystallization to form cubic single crystals, (*e*–*h*) formation of thin FeS_2 plates as a result of attachment and recrystallization processes.

It was shown[141] that nanoplates can form as a result of oriented attachment of quasi-one-dimensional nanostructures. In particular, such mechanism is involved in the growth of nanoplates of tungsten bronze K_xWO_3. Varying the temperature of K_xWO_3 synthesis led to the changes in the shape of synthesized particles: at low temperatures one-dimensional nanostructures were formed, at high temperatures the structures were two-dimensional. Note that the attachment of parallel-oriented one-dimensional nanoparticles to form 2D structures is apparently quite a frequent phenomenon.[142]

Three-dimensional nanostructures. Three-dimensional oriented attachment makes it possible to synthesize materials with unique microstructure. Particularly, this method was successfully used in preparation of porous single crystals of different composition and morphology such as the crystals of TiO_2,[143] $SrTiO_3$,[144] Ag_2O,[145] CeO_2.[92] The oriented attachment was used for producing hollow octahedral SnO_2 particles,[146] $BiVO_4$ spheres,[147] α-Fe_2O_3 polyhedrons,[148] CeO_2 spheroids,[149] MnO_2 nanorods,[150] ZnO pyramids.[151] Studying the mechanism of formation of these objects[146, 152] has shown that it involves several stages including formation of two-dimensional building blocks according to the model of oriented attachment, their assembling into bulk structures and subsequent recrystallization by the dissolution–crystallization mechanism. It is noteworthy that three-dimensional attachment can produce crystals with a habitus matching the Curie–Gibbs–Wulff rule. For instance, anatase nanocrystals are aggregated to afford porous microcrystals shaped as the tetragonal bipyramid typical of this phase.[135]

Like two-dimensional structures, the three-dimensional ones can form by various routes including

2 D → 3 D

1 D → 3 D

0 D → 3 D

The polyhedral TiO_2 crystals mentioned above are formed by the attachment of planar square blocks consisting of aggregated primary TiO_2 particles.[153] Cubic α-Fe_2O_3 crystals grow due to attachment of α-Fe_2O_3 nanorods.[154] Finally, silver nanoprisms are formed as a result of attachment of isotropic spherical silver nanoparticles.[155]

It was shown that oriented attachment may produce dendrites.[156, 157] It deserves mention that when dendrites grow by the classical mechanism, the neighbouring branches are often misoriented by several degrees as a result of bending and shifting during the crystallization. Dendrites formed by attachment of nanoparticles are characterized by the precise mutual orientation of branches (although this rule is not universal, *e.g.*, see Ref. 158). Note that oriented attachment is used more and more often in the synthesis of so-called multipods, *i.e.*, symmetrical branching crystals

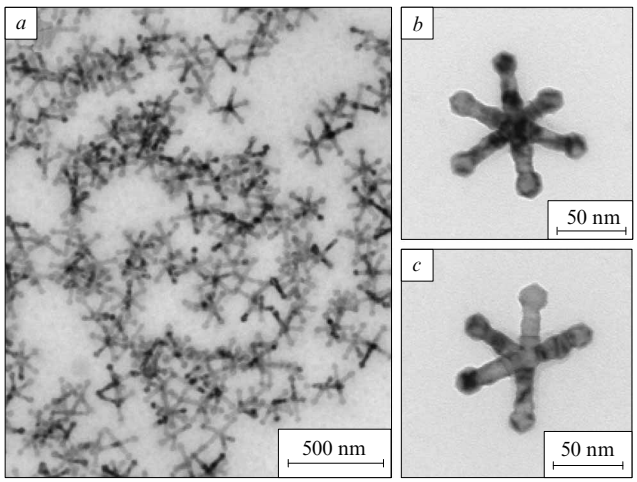


Figure 13. Images of multipods (*a*), hexapod (*b*) and pentapod (*c*) of manganese monoxide.[159]

(Fig. 13). Li *et al.*[160] surveyed in detail the mechanisms of formation of such nanostructures.

Relatively recently, it was shown that oriented attachment of nanoparticles can occur even if the nanoparticles have different chemical or phase composition. In particular, this method was used to prepare Ag_2O nanoparticles coherently attached with sodium titanate nanorods.[161] This phenomenon is of considerable interest from the viewpoint of targeted design of nanocomposites.

Breakdown of symmetry upon oriented attachment. Oriented attachment can produce unusual asymmetrical nanostructures which are difficult to obtain by other methods. One interesting example is the formation of conical silver metal nanoparticles on heating of an aqueous solution of silver trifluoroacetate in the presence of polyvinylpyrrolidone and polyethylene glycol (Fig. 14).

The silver nanocones grow according to the mechanism of oriented attachment in the longitudinal direction and the Ostwald ripening mechanism in the transverse direction.[162] When a relatively stable precursor, CF_3COOAg, is used, the size distribution of primary particles turns out to be sufficiently wide. When a coarse (and more stable) primary particle is attached to one end of the growing particle, the growth in this direction stops and the lateral growth becomes predominant, which ultimately produces a cone.

It was found relatively recently that in the presence of chiral biomolecules, *e.g.*, L-glutamic acid, asymmetrical particles can form; the degree of asymmetry increases with the synthesis time.[163] Probably, this is due to the specific adsorption of biomolecules on the steps of growth, which directly affects the crystal morphology (Fig. 15).

Viedma *et al.*[164] were the first to demonstrate that oriented attachment can result in selective crystallization of enantiomers from racemic mixtures. Note that Ostwald ripening can also lead to this result.[165, 166] For example, heating of a saturated aqueous solution containing the racemic mixture of fine $NaBrO_3$ crystals induces their growth by the mechanism of Ostwald ripening followed by attachment.This affords aggregates measuring 200–500 μm which consist of numerous bridged crystallites formed due to dissolution–crystallization processes.[167] The overwhelming majority of aggregates consists of a single type of crystallites, either left- or right-handed crystals (Fig. 16). The angle of misorientation of individual crystals in the aggregate is several degrees.

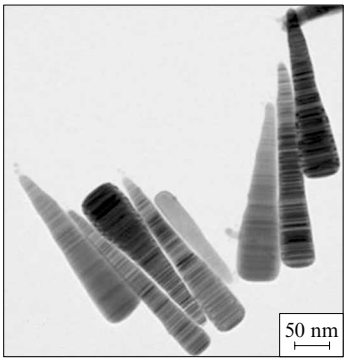


Figure 14. SEM image of asymmetrical silver nanoparticles formed by the mechanism of oriented attachment.[162]

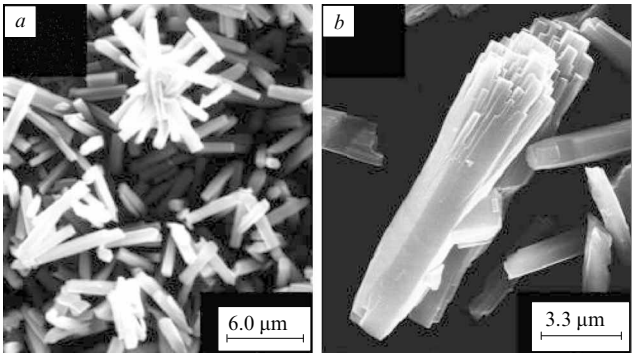


Figure 15. Microimages of hydroxyapatite samples synthesized under hydrothermal conditions in the absence of additives (*a*) and in the presence of L-glutamic acid (*b*).[163]

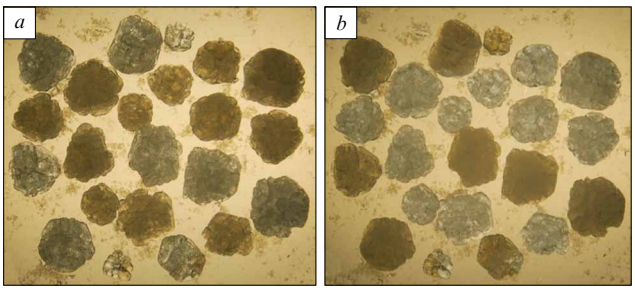


Figure 16. Images of aggregates containing several thousands of D- (*a*) and L-crystallites (*b*) of $NaBrO_3$ collected with the use of polarizing filters.[164]
The images were obtained at a relative rotation of polarizing filters by several degrees in the opposite directions. The uniform colour of aggregates (light or dark) suggests that each aggregate consists of one type of crystals. Aggregate size ~5–10 mm.

III.5. Control over the structure of materials formed by the oriented attachment mechanism

To control the structure of materials formed by the oriented attachment mechanism, besides the chemical factors, it was proposed to use various types of external impact on the reaction medium. One of the most efficient methods of this sort is ultrasonic treatment. It is well known that running acoustic waves of sufficiently high intensity (usually > 1 W cm^{-2}) through a liquid may induce several physicochemical processes, the key process being the cavitation, *i.e.*, formation, growth and collapse of vapour–gas bubbles.[168–170]

The size of particles formed in the ultrasonic field is usually very small. Hence, ultrasound can be used for the indirect action on the mechanism of nanoparticle attachment thus providing crystals with the desired size-dependent properties. Particularly, the small crystal size of ferroelectrics favours their spontaneous polarization, which results in oriented attachment of particles due to the dipole–dipole interaction. The corresponding numerical experiments on the sonochemical synthesis of barium titanate have been reported.[171, 172]

The collapse of cavitation bubbles near the interface generates intense microflows and shock waves in the liquid,[169] which lead to cavitation erosion. This also

increases the collision frequency of particles in the suspension which enhances the probability of their oriented aggregation followed by merging. Such an effect probably took place in the synthesis of Sb_2O_3,[173] CuO[174] and $BiPO_4$[175] nanostructures and also $PbWO_4$ dendrites.[176–178] Under certain conditions, shock waves may result in deaggregation of oriented nanoparticles.[179, 180] The possibility of the oriented attachment mechanism is to a large extent determined by both the ultrasound power and the presence of surfactants in the reaction medium.[181]

To date, the criteria that determine the regularities of particle growth in cavitating liquids have not yet been formulated. This is why of special interest would be the studies of electrokinetic phenomena and the state of the electric double layer under the conditions of well-developed cavitation. Such studies have never been carried out, although certain experimental data are available.[182]

Other methods of controlling the process of oriented attachment have also been reported. For instance, it was proposed to carry out the synthesis in the electric field at different voltages between the electrodes.[145] Of no less importance are the methods based on the effect of external magnetic fields or hydrodynamic shear flows. In individual cases, an additional external impact on the reacting systems can be used not only for the targeted change of the dynamics of particle growth, but also as a tool for studying the oriented attachment. Particularly, being a high-rate, inertia-free and homogeneous method, heating in the MW field can be used in elucidating the regularities of initial stages of oriented attachment of crystals. For instance, such studies were accomplished with the aim of analyzing the growth mechanism of zinc oxide nanorods[183] and $NaTi_3O_6(OH)\cdot 2\,H_2O$ nanowires.[184]

III.6. Modern lines of research in the field of the mechanism and kinetics of oriented attachment of nanoparticles

Detailed studies of the growth regularities of ZnS nanoparticles under hydrothermal conditions were carried out by the HR TEM method.[185] Based on kinetic data, it was found that the oriented attachment of particles in the presence of organic ligands can follow a sufficiently complicated scenario involving both the relatively fast stage of oriented attachment as such and the subsequent slower stage of particle growth by the mechanism of dissolution–crystallization. It was shown[68] that the mechanism of growth for α-Fe_2O_3 nanoparticles under hydrothermal conditions also includes two stages, namely, the oriented attachment of α-Fe_2O_3 crystals by the {104} fases to afford spheroidal aggregates and subsequent recrystallization of the latter to form rhombohedral particles. A similar sequence of particle growth was also postulated in other studies (*e.g.*, see Refs 152, 186, 187). Moreover, kinetic analysis often allows these two growth stages to be clearly separated. It is interesting that according to certain data,[188] the growth of Sm_2O_3 nanorods can proceed also in the reverse sequence, namely, first by the mechanism of Ostwald ripening and then by the mechanism of oriented attachment. Such order of growth stages was also observed later for β-FeOOH nanorods.[189]

It was shown[190] that oriented attachment can proceed according to two fundamentally different schemes:

— by mutual rotation of particles to diminish their misorientation;

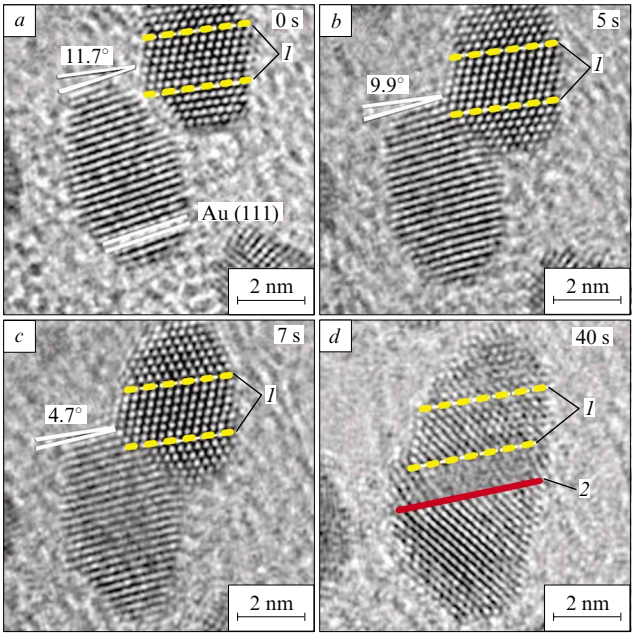


Figure 17. Microimages illustrating the attachment of gold nanoparticles accompanied by their rotation.[190]
(*a*) Two nanoparticles that have come into contact at the angle of 11.7°; (*b–d*) rotation of nanoparticles to diminish their misorientation. Yellow and red dashed lines indicate the position of twinning boundaries that have existed in the original particles and are formed as a result of their attachment.

— through atom-by-atom reorientation upon displacement of grain boundaries after the agglomeration of particles (recrystallization).

Both schemes were observed experimentally in the *in situ* HR TEM studies of the coalescence of gold nanoparticles on a graphene support (Figs 17, 18). The rate of reorienta-

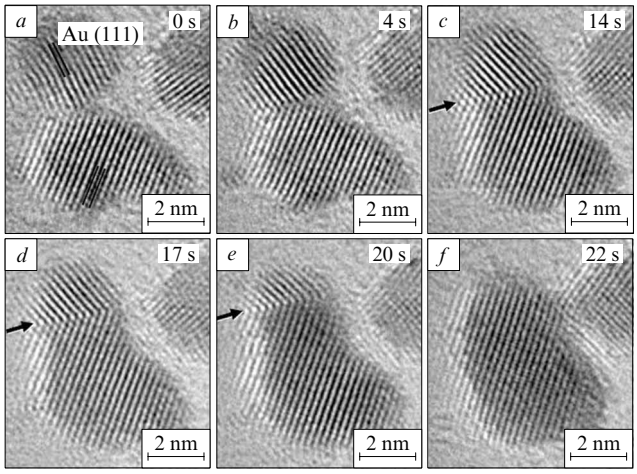


Figure 18. TEM images illustrating the attachment of gold nanoparticles accompanied by migration of the grain boundary.[190]
(*a*) Mutual approach of two particles, (*b*) formation of a bridge between particles, (*c–f*) migration of the grain boundary towards the edge of a particle formed by attachment of primary particles.

Table 1. Activation energy (kJ mol^{-1}) of the oriented attachment and Ostwald ripening of CdTe nanoparticles.[191]

[CdTe] /mol $litre^{-1}$	Oriented attachment	Ostwald ripening
0.3	117.8 ± 4.9	87.4 ± 3.3
0.1	98.5 ± 4.2	86.6 ± 3.2
0.033	85.7 ± 3.1	87.3 ± 3.8

tion in the case of relative rotation of particles is inversely proportional to their size.

An experimental study of the effect of concentration of primary particles on the kinetics of their oriented attachment, which was accomplished for CdTe quantum dots stabilized by thioglycolic acid, has shown[191] that their growth comprises two stages, where the first stage proceeds as the oriented attachment and the second stage is the Ostwald ripening. According to the kinetic analysis, the rate constant and activation energy for the oriented attachment depend substantially on the concentration of nanoparticles (Table 1). This is quite uncommon because the rate constant is usually independent of the reactant concentration. The existence of such dependence is associated with two factors, namely, the desorption of the stabilizing agent (thioglycolic acid) from the CdTe particle surface upon dilution of colloid solutions and the simultaneous changes in the zeta potential of particles, which can affect the nature of the electrostatic interaction between them.

In several studies it was shown that the growth mechanism of nanoparticles can be controlled by appropriate choice of the initial substance. Particularly, according to a research,[192] the growth of cerium dioxide nanoparticles during their hydrothermal synthesis in the presence of sodium oleate proceeds by the oriented attachment mechanism if the starting reactant is a salt of trivalent cerium and by the Ostwald ripening mechanism if the starting reactant is a salt of tetravalent cerium. Note that switching of the growth mechanism gives rise to nanoparticles that substantially (virtually twofold) differ in their size.

Particle attachment can be controlled by varying the composition of their ligand coatings. Thus by varying the concentration of counter-ions, one can synthesize 1D, 2D or 3D nanostructures, particularly, $Bi_5O_7NO_3$ nanorods or nanoplates, under the same conditions.[193] Vivid and interesting examples illustrating the advantages of this approach are known.[194, 195] It was found that the slow removal of oleic acid (*e.g.*, with the use of dimethyl formamide) from the surface of cuboctahedral PbS quantum dots deposited on various supports results in their attachment to afford structures with two-dimensional lattices of square symmetry (Fig. 19). In contrast to mesocrystals with primary particles held together by van der Waals forces,[3] in the synthesized structures, strong chemical bonds are formed between the particles. According to experimental data,[194] the removal of ligands from the surface of PbS particles proceeds selectively from {100} facets, while {111} facets remained shielded, which results in the formation of regular structures. When other solvents possessing lower affinity to oleic acid are used (water, acetonitrile, diethylene glycol, methylformamide), neither the mentioned ordering nor attachment of particles are observed.

One can also control the attachment of particles and the symmetry of resulting structures by varying the concentration of quantum dots in the original colloid solution and the synthesis temperature.[141, 195] Thus either nanowires or planar hexagonal and square lattices were synthesized from one and the same initial monodisperse PbSe particles shaped as cuboctahedra (Fig. 20). Obviously, the mentioned synthetic parameters affect the equilibrium of the processes of ligand sorption–desorption from various facets of the particles thus providing control over the particle attachment.

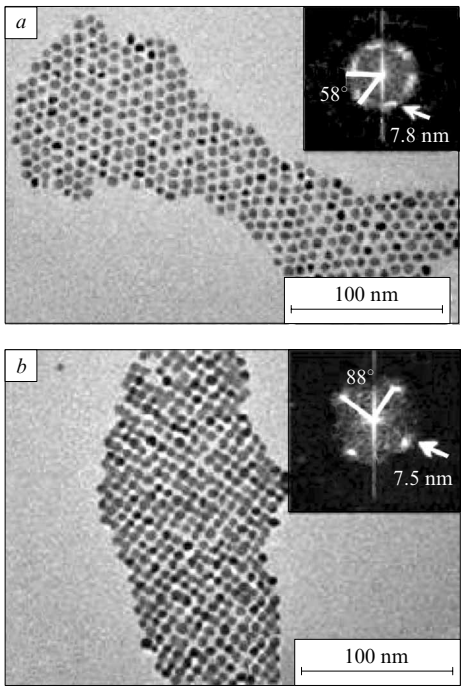


Figure 19. TEM images of films of PbS quantum dots before (*a*) and after (*b*) their treatment with dimethylformamide.[194]
The insets show the results of Fourier transform of images demonstrating the transition from hexagonal to cubic packing of quantum dots.

Zheng *et al.*[196] studied *in situ* the growth of individual platinum plates in a colloid solution by the HR TEM method in a specially designed cell. They have demonstrated that the particles grow simultaneously according to both the classical and non-classical mechanisms. In the former case, the particle size increased gradually; in the second case, it increased in steps. The non-classical mechanism included periods of growth and structural relaxation which involved the partial recrystallization of particles. The relaxation time was experimentally shown to be proportional to the third power of the particle size.

A similar liquid cell was used to examine the growth dynamics of nanoparticles of iron oxide hydroxide $5\,Fe_2O_3 \cdot 9\,H_2O$.[197] It was shown that in this case, the growth also proceeds simultaneously by two mechanisms. Time-resolved studies made it possible to find that before their final attachment, the individual nanoparticles rotate and move chaotically coming into contact with one another many times in different sites (Fig. 21). Irrespective of the number of collisions, in the moment of complete attachment, the particles acquire the same crystallographic orientation or form a twinning defect. Analyzing the character of their motion has shown that as the particles approach

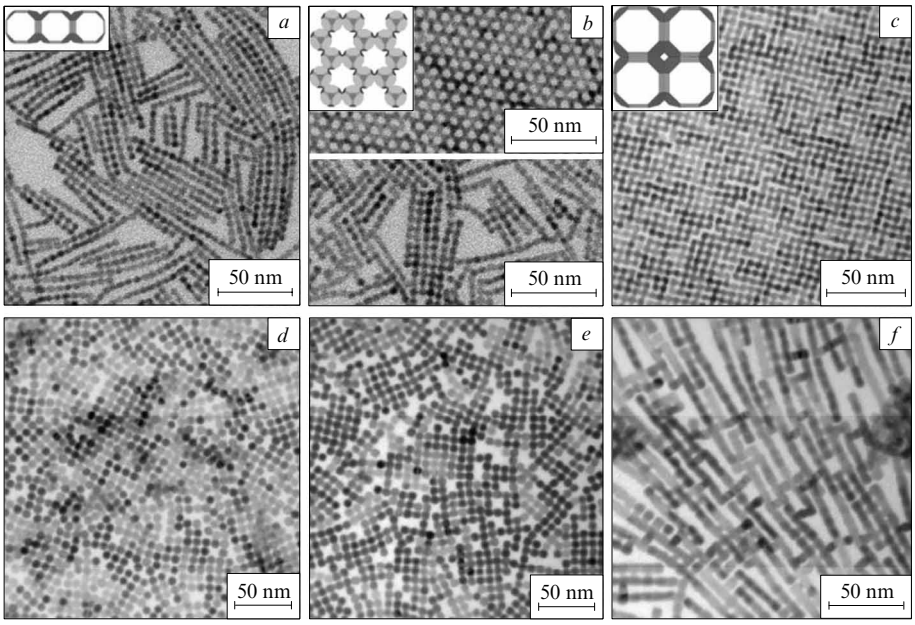


Figure 20. TEM images illustrating the possibility of conrolling the attachment of PbSe nanoparticles by varying their concentration (*a*–*c*) at the synthesis temperature of 50°C and by varying the synthesis temperature (*d*–*f*) at the particle concentration of 14×10^{-7} mol litre^{-1} (Ref. 195).
Particle concentration /10^{-7} mol litre^{-1}: (*a*) 7, (*b*) 11.3, (*c*) 28; synthesis temperature /°C: (*d*) 45, (*e*) 100, (*f*) 140. The insets illustrate different structures: linear (*a*), honeycomb (*b*) and two-dimensional plates with the square symmetry (*c*) formed from nanoparticles.

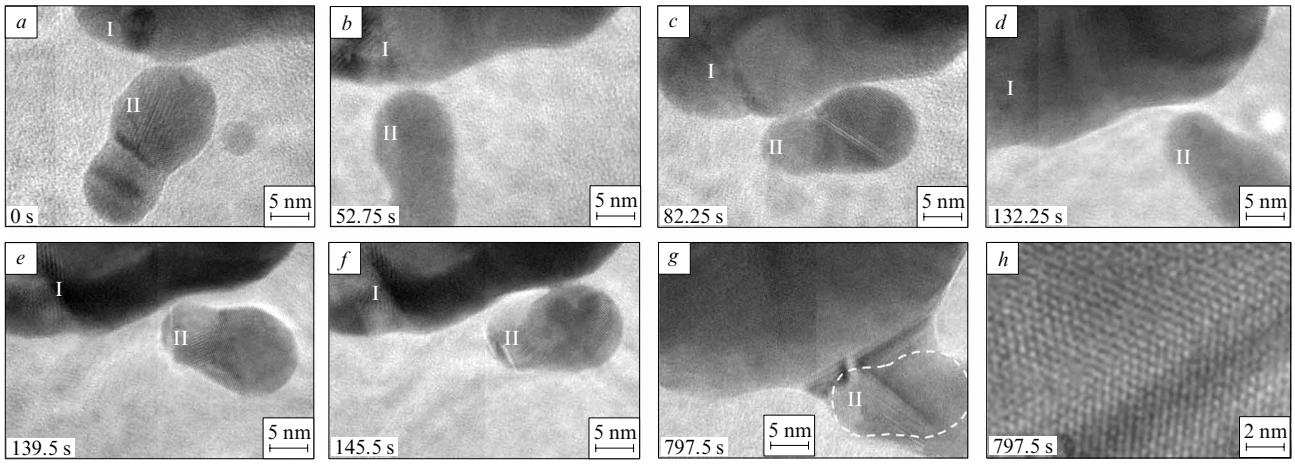


Figure 21. TEMimages reflecting the typical dynamics of oriented attachment of nanoparticles (*a*–*g*) and primary particle interface (*h*).[197]
Particles I and II many times come into contact with one another by different points before being finally attached to one another. Dashed curve outlines the primary particle II.

one another, the rates of their translational and rotational motion increase by a factor of 2–4. It is noteworthy that as the fine particles approach coarse ones, they can dissolve even though they have been stable before. Thus, the Ostwald ripening can also be observed in those cases where the oriented attachment of nanoparticles is the predominant mechanism.

In a study of how the ligand (oleylamine) concentration affects the growth of FePt nanoparticles, it was found [198] that the following three processes occur when the ligand is present in a moderate concentration (20%):

— formation and growth of primary FePt particles,

— attachment of primary particles to afford FePt nanowires,

— shrinkage or destruction of nanowires to form nanoparticles with a wide size distribution.

As the oleylamine concentration increases to 30%, the FePt nanowires formed by a similar mechanism become stable and are no longer destroyed. A further increase in the stabilizing agent concentration to 50% suppresses the attachment of primary particles.

Table 2. Experimental data on the duration of oriented attachment processes in the liquid phase.

Objects	Investigation method	Duration of attachment /s	Ref.
Nanorods and nanoplates of $WO_3 \cdot H_2O$	*ex situ*	$\sim 10^2$	93
AuCu nanowires	*ex situ*	$10^3 - 10^4$	105
ZnO nanorods	*ex situ*	$\sim 10^2$	183
Isotropic Au nanoparticles (see [a])	*in situ*	$10 - 10^2$	190
Isotropic Pt nanoparticles	*in situ*	~ 10	196

[a] Growth on a graphene support.

It should be noted that the use of liquid cells in HR TEM becomes more and more popular for analyzing *in situ* the growth processes of metal nanoparticles according to classical and non-classical mechanisms.[199] Several original cell designs have been developed including a cell with graphene windows which provides the best spatial resolution.[200]

Of considerable interest are the data on the characteristic time of oriented attachment processes. Table 2 shows the corresponding generalized results obtained by studying the formation of various materials both *in situ* and *ex situ*. Although the available data are rather scarce, it can be assumed that anisotropic structures are formed at a lower rate than isotropic structures; this is what is to be expected because of geometrical reasons.

Shen *et al.*[201] studied how the size factor affects the growth of particles according to the oriented attachment mechanism. As the starting particles, they used virtually monodisperse copper metal nanoparticles with the characteristic size of 2.2, 3.4 and 5.2 nm, which were subjected to solvothermal treatment. It was found that the smaller particles were aggregated to form nanorods or nanodisks depending on the treatment temperature, whereas the coarser particles were combined into irregular aggregates. This qualitatively agrees with the results of molecular dynamics simulations[202] according to which the size of particles determines their trend towards reorientation.

According to calculations,[203] the size of nanoparticles has virtually no effect on the type of facets they are atttached to; the key role is played by their crystal structure. In the general case, the advantage in energy of the oriented attachment of particles over the Ostwald ripening is determined not only by the decrease in the specific surface area but also by interatomic interactions in the growing crystal.[203] Based on the results of molecular dynamics simulations, it was shown that the interaction between nanopaticles in a colloid solution is determined also by the affinity of particles to the solvent, their shape and surface topography.[204–208] Solvophilic particles can be either attracted to one another or repelled from one another depending on the distance between them and mutual orientation. Thus, in solution, colloid particles rotate while approaching one another in order to minimize their free energy. The regularly shaped particles (especially coarse particles with clear-cut faceting, *e.g.*, cubic) demonstrate the most pronounced tendency for mutual orientation.

Baumgartner *et al.*[209] have noted that according to the Ostwald rule of stages, the formation of thermodynamically stable phases from solution should be preceded by the formation of metastable intermediates including amorphous ones. A cryogenic TEM study of the mechanism of formation and growth of magnetite nanoparticles from a solution containing iron(II) and iron(III) chlorides revealed two main stages, namely, fast formation of virtually monodisperse (~ 2 nm) primary particles followed by their aggregation and attachment to afford spheroidal magnetite particles of 10–15 nm size. In the course of attachment of primary particles to coarse particles, the size of the former somewhat decreases due to either dissolution or the olation and oxolation processes.

Based on the analysis of experimental data,[209,210] a general model that describes the known scenarios of crystallization was proposed (Fig. 22). According to this model, the following routes are possible for the crystal phase formation:

I — atoms (molecules) join to form an amorphous bulk phase;

II — the crystal phase is formed directly from atoms (molecules);

III — attachment of primary amorphous or crystalline particles (clusters) affords the amorphous phase;

IV — attachment of primary amorphous or crystalline particles (clusters) affords the crystalline phase.

Note that in practice, routes *II* and *IV* are encountered most often.

A direct result of oriented attachment of particles may be the change in their phase composition; particularly, the attachment of ZnSe quantum dots to the sphalerite structure affords nanorods with the wurtzite structure.[211]

Until recently, the known examples of oriented attachment pertained to inorganic materials. In 2012, it was demonstrated for the first time[212] that organic tubes can undergo oriented (end-to-end) attachment. It is interesting that these nanotubes were X-ray amorphous; hence, it can be assumed that they were formed by route *III* (see Fig. 22). The reasons for the breakdown of symmetry and the formation of an ordered structure upon attachment of primary amorphous particles are not quite clear so far and require special investigation. Also note that the control over the microstructure of organic materials with the use of

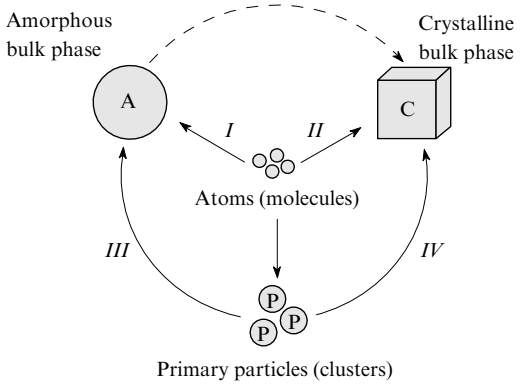


Figure 22. General scheme of the crystal growth process.[209] For *I*–*IV*, see text.

oriented attachment processes is a promising and insufficiently explored research area.

IV. Conclusion

The numerous experimental data demonstrated the abundance of the non-classical mechanism of crystallization. It deserves mention that this mechanism does not contradict the classical models of crystal growth but supplements them. Indeed, the growth by the Burton – Cabrera – Frank mechanism requires the presence of screw dislocations. For the majority of materials, the size of a stable dislocation loop lies in the range of 10 – 100 nm,[213] a dislocation within the loop being unstable for particles with the size below this value. Probably, it is due to the oriented attachment that nanoparticles can reach the necessary critical size. Moreover, the crystallographically inaccurate attachment serves as the source of dislocations and twinning defects in nanoparticles and provides the basis for the subsequent transition to the classical growth mechanism.

Oriented attachment is one of the key mechanisms of biomineralization processes that form the structure and account for the unique physicochemical properties of natural materials.[214 – 217] It is not surprising that quite a number of fundamental data on the peculiarities of oriented attachment were first obtained by mineralogists.

Building the models that would allow one to pass to quantitative description of the dynamics of oriented attachment of nanoparticles is of the key importance for the development of the theory of this process. Some attempts along this line have already been undertaken (*e.g.*, see Refs 218 – 221); however, this problem is far from its final solution as yet.

From the point of view of material science, of considerable interest is the analysis of mechanisms that induce one or another type of faceting (quite often untypical of the given substance) as well as the breakdown of symmetry for crystals formed as a result of oriented attachment of nanoparticles. The effect of the growth medium on the oriented attachment remains virtually unstudied; it is often implied that in contrast to the classical crystallization, the characteristics of the growth medium play only a secondary role, which apparently is not the case. Thus, under certain conditions, the oriented attachment can be reversible: the aggregates can dissociate to the constituent particles which is followed by their secondary assembling to afford structures of different morphology.[125] It is of interest that the oriented attachment of nanoparticles can apparently occur even in extremely viscous media, *e.g.*, in glass.[222, 223]

The growth of crystals by the oriented attachment mechanism can proceed in two considerably different ways. The first mechanism includes attachment of particles with comparable sizes and the second one includes attachment of finer particles to coarser ones. Due to the keen attention paid today to nanomaterials, the well-known examples preferentially illustrate the first route of nanoparticle growth, whereas the second route still requires a more thorough investigation.

Finally, it deserves mention that further studies of the oriented attachment of nanoparticles require the use of modern analytical methods having high spatial and temporal resolution, first of all, electron microscopy and the methods based on the use of synchrotron radiation, including wide- and small-angle X-ray scattering, X-ray absorption spectroscopy, X-ray transmission microscopy, *etc.*[224 – 227] Of no less importance can be the conventional highly sensitive methods used to study the chemical kinetics and thermodynamics, including calorimetric methods, radiochemical methods, *etc.*, which have not been used so far in the analysis of oriented attachment.

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