

Progress of nanocrystalline growth kinetics based on oriented attachment

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The crystal growth mechanism, kinetics, and microstructure development play a fundamental role in tailoring the materials with controllable sizes and morphologies. The classical crystal growth kinetics—Ostwald ripening (OR) theory is usually used to explain the diffusion-controlled crystal growth process, in which larger particles grow at the expense of smaller particles. In nanoscale systems, another significant mechanism named “oriented attachment (OA)” was found, where nanoparticles with common crystallographic orientations directly combine together to form larger ones. Comparing with the classical atom/molecular-mediated crystallization pathway, the OA mechanism shows its specific characteristics and roles in the process of nanocrystal growth. In recent years, the OA mechanism has been widely reported in preparing low-dimension nanostructural materials and reveals remarkable effects on directing and mediating the self-assembly of nanocrystals. Currently, the interests are more focused on the investigation of its role rather than the comprehensive insight of the mechanism and kinetics. The inner complicacy of crystal growth and the occurrence of coexisting mechanisms lead to the difficulty and lack of understanding this growth process by the OA mechanism.

In this context, we review the progress of the OA mechanism and its impact on materials science, and especially highlight the OA-based growth kinetics aiming to achieve a further understanding of this crystal growth route. To explore the OA-limited growth, the influence of the OR mechanism needs to be eliminated. The introduction of strong surface adsorption was reported as the effective solution to hinder OR from occurring and facilitate the exclusive OA growth stage. A detailed survey of the nanocrystal growth kinetics under the effect of surface adsorption was presented and summarized. Moreover, the development of OA kinetic models was systematically generalized, in which the “molecular-like” kinetic models were built to take the OA nanocrystal growth behavior as the collision and reaction between molecules. The development of OA growth kinetics can provide a sufficient understanding of crystal growth, and the awareness of underlying factors in the growth will offer promising guidance on how to control the size distribution and shape development of nanostructural materials.

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1. Introduction

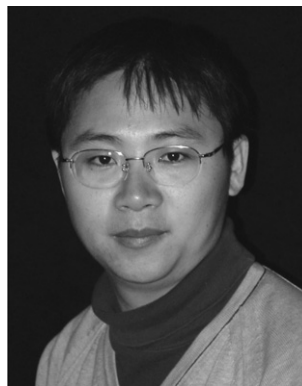
Nanoscale materials are defined as materials having at least one dimension in the 1–100 nm range, in which nanocrystals are the major investigated subjects. Since Gleiter and coworkers



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emulsions and their effects on the nucleation and growth of nanocrystals.

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successfully synthesized Fe nanoparticles in 1984,^{1,2} nanostructural materials have received extensive interest for their unique and fascinating properties and potential applications that are superior to their bulk counterparts. For example, semiconductor nanocrystals have exhibited a wide range of size-dependent properties for optics and electricity.³⁻⁵ The fundamental characteristics from phase stability to electronic structure can be influenced by the size and surface absorption status of nanoparticles.⁶⁻⁸ A detailed investigation of quantum size effects requires the preparation of nanoscale materials with a controllable size and morphology. The synthetic approaches for preparing nanoscale materials are various, and mainly include chemical methods,^{9,10} physical techniques,^{11,12} and biological means.¹³ Among them, the advantages of wet chemical methods are that the synthesis can be realized in a massively parallel fashion and with a simple facility (*e.g.* hydrothermal conditions). But its disadvantage mainly lies in that the size and shape are difficult to control in the process, as they undergo rapid nucleation and growth, readily impacted by surrounding interactions. Especially for nanostructured materials synthesized by chemical synthesis, the study on the crystal growth kinetics shows its scientific and practical significance for understanding and controlling the evolution of size and shape.

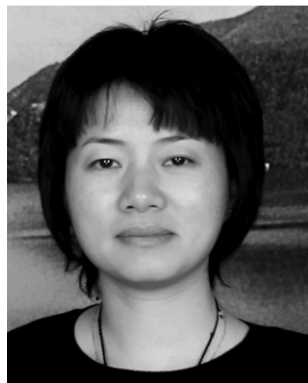
Detailed investigations on the nanocrystalline growth mainly involve the growth mechanisms, the kinetic rules of size and morphology, and the accompanying phase transformation. By observing the microscopic structures of nanocrystals, the growth mechanisms will be found and judged. Then, the corresponding growth kinetic models will be proposed to describe and explain the crystal growth behavior. An understanding of the factors that affect crystal growth kinetics and the microstructure development in nanocrystals is fundamental to tailor new types of nanostructures and control material properties. Accordingly, research in the field of crystal growth kinetics attracts increasing attentions.^{7,14-16}

As classical growth kinetics, the OR theory has shown great progress made in the past forty years or more. Various theories have been developed to describe and predict this atom-by-atom growth process, and the agreeable results between experimental and theoretical work can be well achieved.¹⁷ When the crystal size decreases to the nanometre level, in some circumstances, the crystal growth may be dominated by the newly developed OA

mechanism,¹⁸ the direct self-organization of two particles into a single crystal by sharing a common crystallographic orientation. In contrast to the classical crystal growth pattern, the OA mechanism shows a peculiar growth pathway and characteristics, even contradicting the former. The aggregation-based growth mode attracts the interest of many researchers and presents its significant role in the construction and formation of nanostructural materials.^{16,19,20} As the OA is the assembly of primary particle units, the way of bottom-up fabrication can produce the novel objects with versatile properties, probably retaining the original structures and properties of their building blocks. It will give us a clue to tailor the products by tuning the raw materials. Also, the OA is an effective approach in favor of manufacturing anisotropic nanostructures, such as particle attachment always generating one-dimension nanowires or nanorods in one orientation.^{4,21,22} As for the crystal growth process, the unique mechanism can give rise to the critical information related to the shape and size evolution distinctively away from the classical growth pathway.

Extensive reports declare the importance and versatility of the OA mechanism for the material design and preparation, while detailed and in-depth investigations of the physical basis behind the OA-limited process are absent currently. The main challenge in exploring the OA mechanism is the acquisition of direct data and evidence from the complicated crystal growth process, especially on a nanoscale, which yields the difficulties of building the growth kinetic models and fitting the experimental data. Inspiringly, a series of work on the OA-based growth kinetics has been gradually carried out with efforts to explain the process in theory. The first OA kinetic model was developed in 2003,²³ which takes the direct coalescence of particles as the reaction between the molecules and well fits the experimental results of particle size *vs.* time. After that, Penn¹⁹ and Ribeiro *et al.*²⁴ respectively advanced the models from the viewpoint of the electrostatic interaction and colloid coagulation. In the view of aggregation, this crystal growth model is similar to the Smoluchowsky theory,²⁵ which has been widely used to explain and fit the aggregation of molecules and colloids, and to describe the dynamical nucleation process. Generally, it was found that the mixed mechanisms coexisting in the growth bring the difficulty to obtain the systematical experimental data (such as the growth rate) and hinder the progress of the OA growth kinetics.²³

In the study on OA growth kinetics, the effects of surface adsorption and surface charge were discussed to be the important factors for the crystal growth process and the OA mechanism. It is viewed that by adding ligands and passivating agents or by changing the particle surface one can control the growth by the OA mechanism.^{19,23} It was also reported that the nanocrystal growth rate is dependent on the adsorption of anions and a stronger adsorption leads to a slower OR growth rate.^{26,27} It is known that in nanoscale systems, the surface contributions to the total energy become increasingly important as the particle size decreases, even determining the structures and phase stability.⁶ The remarkable effects of surface functionalization with various molecular weight ligands may bring different assembly behaviors.²⁸⁻³⁰ Nanocrystals have a higher surface energy, which facilitates the “reaction” on the surface, such as the direct bonding and crystallization between particles.¹⁸ Factors that



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directly modify the surface of nanocrystals will be a promising way to direct and mediate the crystal growth modes.

In this review, we summarize the progress of the OA-based growth kinetics, highlighting recent endeavours on the nanocrystal growth kinetics under the strong organic/inorganic surface adsorption, and the corresponding OA kinetic models. The introduction of the strong surface adsorption aims to adjust the crystal growth mode and realize the growth *via* the solo OA mechanism, which will simplify the experimental investigation for theoretical fitting. The advance in kinetic models can provide a comprehensive understanding of the OA-based growth behavior, as well as a potential guide to find a full satisfactory approach for the growth kinetics. The studies on the growth kinetics also offer the physical and chemical parameters and information that is meaningful for the control of the growth rate and size distribution in the system.

2. The classical growth kinetics for coarsening—Ostwald ripening

When giving an overview for the crystal growth kinetics, we can't overlook the influence and power of the classical kinetic model—Ostwald ripening (OR) mechanism.^{31–33} Early studies on the kinetic model for coarsening of crystals were almost based on the OR mechanism, which involves the growth of larger particles at the expense of smaller ones. The driving force for this process is the decrease in total surface free energy. According to the Gibbs–Thomson equation,³⁴ the equilibrium solute concentration at the surface of larger particles is lower than that of smaller ones and the resulting concentration gradients lead to solute ions flowing from small particles to larger ones. The coarsening mechanism is often controlled by the diffusion, particle growth *via* addition of ions to the particle surface from solution. Fig. 1a illustrates the crystal growth *via* the OR mechanism. The classical kinetic model for the OR mechanism is known as the LSW model which is based on the Gibbs–Thomson equation.^{33,35} The general kinetic equation for these cases can be written as:

$$\bar{D}^n - \bar{D}_0^n = k(t - t_0) \quad (1)$$

where \bar{D} and \bar{D}_0 are the mean particle sizes at time t and t_0 . k is a temperature-dependent material constant, and n is an exponent relevant to the coarsening mechanism. For example, for $n = 3$, the most often case, the coarsening kinetics are controlled by the

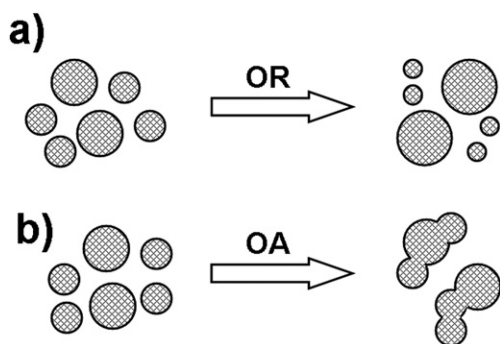


Fig. 1 Scheme of nanocrystal growth controlled by: (a) Ostwald ripening mechanism; (b) oriented attachment mechanism.

volume diffusion of ions in the matrix.^{31–33} From eqn (1), it can be seen that the growth curve of size *vs.* time fits the parabola, and the crystal size increases continuously with time increasing.

The OR mechanism has been used widely to describe and explain the crystal growth of particles with a relatively large size in solution. Experimentalists have confirmed the validity of the LSW theory.¹⁷ Though the OR growth kinetics tend to be satisfactory, some small disagreements between experimentally reported particle distribution and that predicted by the OR theories, still remain. So, in understanding the OR mechanism, more experimental and theoretical work is necessary in this field. In recent years, with the development of research in the nano-scale regime, findings in crystal growth often cannot be explained and fitted by the OR kinetics, especially to nanocrystals with a relatively small size. The typical cases are listed as follows.

(i) The crystal growth curve of particle size against time cannot be fitted properly by the LSW model. Peng *et al.* have reported the “focusing” of size distribution in the nanocrystal growth, and under these conditions, the smaller nanocrystals grow faster than the larger ones.³⁶ The result is obviously inconsistent with the OR theory. Previously, it was found that using eqn (1) to fit the first stage of growth during hydrothermal coarsening of mercaptoethanol-capped nano-ZnS yielded an exponent with no physical meaning ($n > 10$).²³

(ii) The crystal growth in solid phases (such as coarsening in air) often cannot be fitted and explained by the OR mechanism.^{37,38} Krill *et al.* found that the crystal growth rate of nanosized Fe (<150 nm) follows a liner relationship with time.³⁷ Other examples demonstrate that the fitting results to the OR theory deviate from the proper physical explanation.³⁸

(iii) Extensive work revealed that all kinds of irregular, even anisotropic morphologies were obtained in the synthesis of nanostructural materials, such as elongated crystals (chains), butterflies, horseshoes, *etc.*^{21,39–43} Moreover, the microstructure features of nanocrystals often exhibit the incorporation of defects, *e.g.*, dislocation and planar defects (twins, stacking faults, *etc.*). These remarkable features scarcely occur in the crystal growth *via* the OR mechanism.

All of the above cases indicate that the growth of nanocrystals is controlled by an alternative mechanism.

3. The oriented attachment (OA) mechanism

In 1998, Penn and Banfield discovered an important crystal growth mechanism named “oriented attachment”.^{18,44} The mechanism involves spontaneous self-organization of adjacent particles, as grown by addition of solid particles to surface, so that they share a common crystallographic orientation, followed by joining of these particles at a planar interface. Crystal growth *via* the OA mechanism often leads to the formation of nanoparticles with irregular shapes by consuming primary nanocrystals as “building blocks”, and the growth rate is size-dependent.^{23,38}

As a non-classical crystallization mechanism,²⁰ it brings much disputation when a newly developed mechanism appears. But after that, as shown in Table 1, adequate experiment observation eliminates the doubt and proves the validity of the OA mechanism. Gradually, the OA mechanism has attracted preponderant interests, for it is fundamental to design and explore materials

Table 1 Typical examples of oriented attachment mechanism reported in recent years (1998–2008)

Year	First-author	Matter	Morphology	Ref.
1998	Penn	TiO ₂	various morphologies	18,39
1998	Scolan	TiO ₂	oriented aggregates	45
1999	Penn	TiO ₂	rutile elbows; anatase twins	46
1999	Penn	TiO ₂	twins; intergrowths;	44
1999	Lee	CeO ₂	twins and octahedral attached across{110}	47
1999	Audinet	CdS/ZnS	rounded particles with dimples and defects	48
1999	Chemseddine	TiO ₂	elongated and corrugated	49
1999	Ricolleau	CdS CdS-ZnS	twins, stacking faults rounded and dimpled shapes	50
1999	de Moor	zeolite	round	51
2000	Zhang	sulfides, oxides	prisms, spindles, needles	52
2000	Nikolakakis	zeolite	round	53
2000	Kuo	α -Ti, TiC	rounded aggregate	54
2000	Wang	Pt	elongated morphology	40
2001	Shen	ZrO ₂	coalescence twins	55
2001	Penn	Fe ₂ O ₃ FeOOH CoOOH anatase	rounded hematite particles irregular feroxyhite plates hexagonal plates Varied shapes	56
2001	Banfield	ZnS	twins, stacking faults, intergrowths; varied morphologies	57
2001	Shen	MCM-41 (silicate)	mesoporous	58
2002	Pacholski	ZnO	nanorods	59
2002	Niederberger	Hematite	rounded hexagonal plates	60
2002	Sampanthar	β -Co(OH) ₂	“butterflies”	41
2003	Guyodo	α -FeOOH	nanorods	61
2003	Nesterova	FeOOH	various	62
2003	Lou	TiO ₂	horseshoes	42
2003	Cozzoli	ZnO	elongated particles	63
2003	Jun	TiO ₂	bullet, diamond, elongated rod	64
2003	Huang	ZnS	irregular-shape	23
2004	Deng	Bi ₂ Te ₃	nanorod	65
2004	Liu	ZnWO ₄	nanorod	66
2004	Tsai	TiO ₂	nanoparticles	67
2004	Adachi	TiO ₂	nanowire	68
2004	He	Co ₃ O ₄	hollow spheres	68
2005	Liu	CdS	rings	70
2005	Wu	ZnO	nanorods	71
2005	Yu	ZnS	nanorods	72
2005	Gehrke	CaCO ₃	hexagon crystals, lens-shaped	73
2005	Cho	PbSe	straight, zigzag, helical, branched, and tapered nanowires; nanorings	74
2005	Zitoun	MnO ₂	multi-pods	75
2005	Cheng	PbMoO ₄	dendrite	76
2005	Frandsen	α -Fe ₂ O ₃	chains	77
2005	Zhang	CuO	ellipsoidal nanoarchitectures	78
2006	Penn	α -FeOOH	nanorods	79
2006	Bao	NdF ₃	plate-built chain	80
2006	Pradhan	CdSe	nanowire	81
2006	Wen	Ag	dendrite	82
2006	Calderone	SrTiO ₃	hexagon	83
2006	Lu	Sb ₂ S ₃	nanorod-bundles	84
2006	Zhang	CuO	shuttle-like	85
2006	Shen	CaCO ₃	olive-shape, lens-shape, hexagonal platelets	86
2006	Lu	Ag	dendrite	87
2007	Deng	Sb ₂ O ₃	nanorods and nanowires	88
2007	Halder	Au	nanowires	89
2007	Portehault	MnO ₂	nanowires	90
2007	Yong	ZnTe	nanowires	91

Table 1 (Contd.)

Year	First-author	Matter	Morphology	Ref.
2007	Klokkenburg	PbSe/CdSe	dipolar nanostructures	92
2007	Ribeiro	TiO ₂ /SnO ₂	heterostructural nanoparticles	93
2007	Du	NiSe ₂	six-horn nanostars	94
2008	Zhang	Au	mesoporous spheres	95
2008	Zhou	CeO ₂	nanoflowers	96
2008	Hawaladar	PbCrO ₄	nanorods	97
2008	Xu	SnO ₂	nanowires	98
2008	Yu	CdSe	nanorods	99

with size- and morphology-controllability. Fig. 1b illustrates the crystal growth *via* the OA mechanism.

Here, we present some selected examples to illustrate the typical OA phenomena. Usually, the crystal growth controlled by the OA mechanism tends to produce peculiar structures and morphologies. As shown in Fig. 2, the anatase nanoparticles assemble into a chain-like single crystalline structure.³⁹ From the view of thermodynamics, combination in a coherent crystallographic orientation will eliminate the interfaces of nanocrystals. Reduction in surface energy in this way is the primary driving force for OA-based growth, though the detailed assembly process between the primary particles is under studied.

This example demonstrates the potential of OA for building anisotropic nanostructures. Other interesting OA examples include TiO₂ nanorods⁶⁴ and PbSe nanowires,⁷⁴ from which we can see that the structures and shapes of primary “building blocks” act heavily on the OA growth and the product materials. As shown in Fig. 3 and 4, the primary unit is a polyhedral nanocrystal. The difference of surface energy at each face leads to the coalescence of primary particles in specific crystallographic orientation, such as the one-dimension growth in [001] of TiO₂ nanorods (Fig. 3) and in [111] of PbSe nanowires (Fig. 4). Furthermore, during the OA growth, the primary units may keep or partially keep the original structure and configuration, which helps us to judge and study the OA growth kinetics.

As the OA mechanism is the direct coalescence of particles, it provides a route for the incorporation of defects, such as twins, stacking faults, and misorientation. The microstructural features and crystal morphology yield important clues to understand the OA mechanism in detail. As shown in Fig. 5, the growth of mercaptoethanol-capped nanosized ZnS is controlled by the OA mechanism.²³ The big single crystal is composed by five small particle units which are signed as A, B, C, D, and E in Fig. 5a. Arrowheads mark indentations, interpreted to be the interfaces between assembly units. The schematic outlined in Fig. 5b

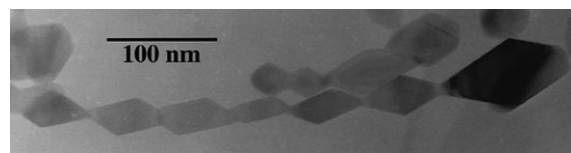


Fig. 2 A chain-like single crystal of anatase that was hydrothermally coarsened in 0.001 M HCl and grown by the OA mechanism. Reproduced with permission from *Geochim. Cosmochim. Acta*, 1999, **36**, 1549. Copyright 1999 Elsevier.

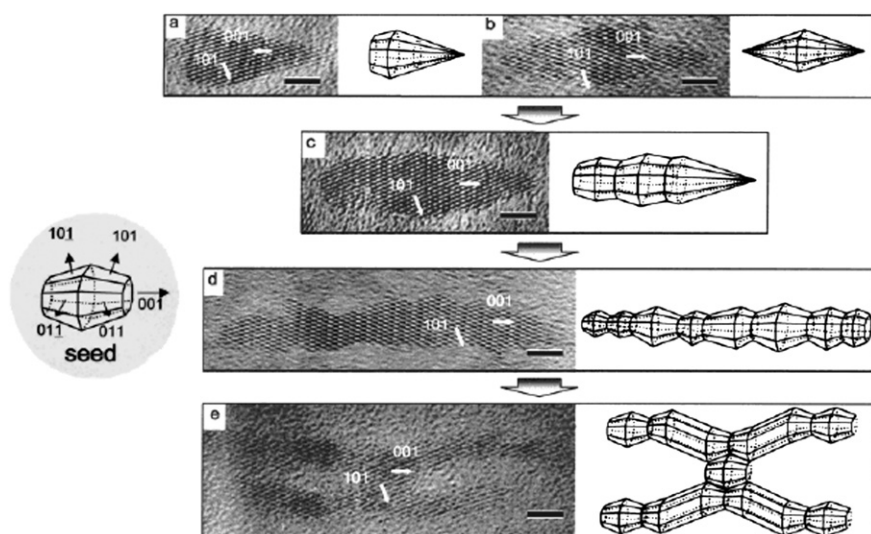


Fig. 3 HRTEM analyses and simulated three-dimensional shape of anatase nanocrystals. (a) A bullet, (b) a diamond, (c) a short rod, (d) a long rod, and (e) a branched rod. The nanorods are formed by the OA mechanism with the primary units of truncated octagonal bipyramid. The long axes of the nanocrystals are parallel to the *c*-axis of the anatase structure in the [001] direction and the branched shape is a result of the growth along [101] directions starting from the hexagon shape. Scale bar: 3 nm. Reproduced with permission from *J. Am. Chem. Soc.*, 2003, **125**, 15981. Copyright 2003 Am. Chem. Soc.

illustrates the features in Fig. 5a and the defects during the OA growth, *e.g.* twin (T), stacking faults (SF). Once formed during the attachment, it is possible to preserve the defects in the following growth process, since transformation from one state into another needs extra energy.⁸⁸ Obviously, these structural defects are the source of nonradiative recombination centers, which reduce the internal quantum efficiency of emission.

The above cases well illustrate the characteristics and roles of OA mechanism in the preparation of nanostructural materials. Plenty of work has emphasized the importance of the OA mechanism in the process of crystal growth and morphology evolution of nanoscale materials which have been summarized in other previous papers,^{20,100,101} but most of the reports only demonstrate the OA mechanism occurring and simply illustrate the ongoing process. The inner complication of the OA mechanism appears to be the major challenge delaying the further advance of the growth kinetics. The exploration of the basic principles of the OA process mainly involves open problems such as: why OA happens? Which factors facilitate OA? What is the OA growth rate? How the assembly units collide and then attach each other, and which one is dominant? How about the microscopic process of the OA, such as the removal of the surface-absorbed molecules and the bonding at the interface? How OA-based growth influences microstructure, shape, phases, and structure–property relationships?

The advance of OA growth kinetics depends on the understanding of the mechanism; inversely, the studies on the OA growth kinetics will offer critical information (*e.g.* the growth rate) to understand the mechanism. As an increasingly important crystal growth mechanism, the OA needs and deserves an in-depth exploration for potentially controlling the development of size and morphology during the growth. Unfortunately, the OA and OR mechanisms often co-exist during the crystal growth.¹⁰² The mixed growth mode brings difficulty for the further

investigation in the growth kinetics. Our preferential work reveals that the effect of surface adsorption should be one of the effective controlling ways to simplify the nanocrystal growth *via* a solo OA mechanism.

3.1 The OA kinetics under the strong surface adsorption

OA crystal growth phenomena have more often been observed for nanoparticles with a relatively small size and weight.^{23,38} Also, the attachments between secondary particles, even larger ones, are observed.^{19,23,102} It was found that under general conditions, OA and OR growth mechanisms occur simultaneously,¹⁰² sometimes accompanied with the phase transformation.¹⁰³ All of these lead to difficulties for investigating this size dependent crystal growth mechanism, especially kinetically.

During systematic studies on the nanocrystal growth kinetics,^{23,104–106} the effect of strong surface adsorption was proved to be the key to thermodynamically hinder the OR growth in the initial stage and attributed to the pure OA growth.

When primary ZnS nanoparticles are free of strong capping ($\text{H}_2\text{O-ZnS}$), the coarsening process in water is consistently controlled by the mixed (OA + OR) mechanism.¹⁰² Though the OA mechanism is major in early stage and the OR acts heavily in the latter, there is no knot to divide the whole growth process, as shown in Fig. 6.

When observing the growth process of mercaptoethanol-capped nano-ZnS (HS-ZnS) coarsening in water,²³ it was discovered that the growth of nanocrystals could be divided into two stages. In the first stage, the asymptotic growth curve cannot be fitted by the OR theory—parabola growth kinetics (see Fig. 7). High-resolution transmission electron microscope (HRTEM) data display the nanocrystal growth limited by the OA mechanism (typical image shown in Fig. 5); the growth curve of two stages show distinct modes and have a dividing knot. These conclude

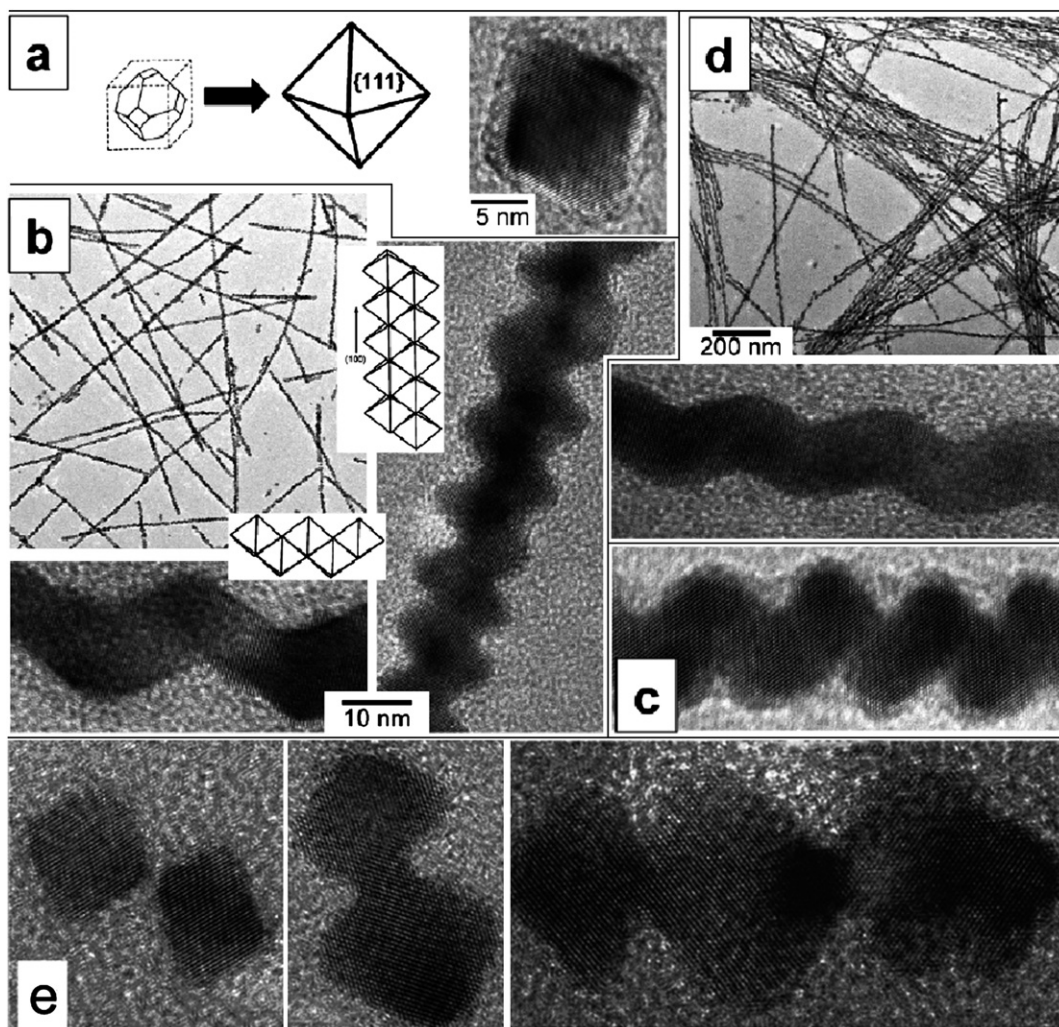


Fig. 4 TEM and high-resolution TEM images of PbSe zigzag nanowires. Single crystal helical PbSe nanowires (3b, 3c, 3d) were formed by the OA mechanism. The primary building blocks are octahedral PbSe nanocrystals (3a) and from Fig. 3e, the assembly process of PbSe nanowires was captured. Reproduced with permission from *J. Am. Chem. Soc.*, 2005, **127**, 7140. Copyright 2005 Am. Chem. Soc.

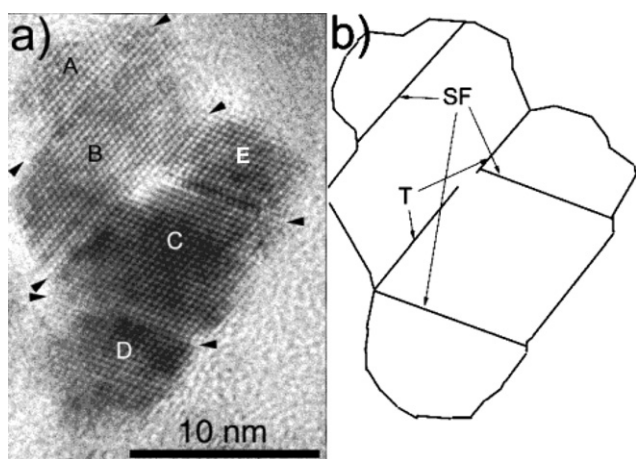


Fig. 5 HRTEM of ZnS nanocrystal formed by the OA mechanism. Reproduced with permission from *Nano Lett.*, 2003, **3**, 373. Copyright 2003 Am. Chem. Soc.

that the growth in the first stage was controlled by the pure OA mechanism. Comparing with the (H₂O-ZnS) system, it can be concluded that the strong surface adsorption of mercaptoethanol is the key to produce the exclusive OA growth.

The surface adsorption of capping ligands resulting in a pure OA growth stage can also be confirmed by the system of thiol-PbS.¹⁰⁴ In this system, the observed growth curves show similar rules as the system of mercaptoethanol-capped ZnS. Also, as shown in Fig. 8, HRTEM data confirm the existing OA mechanism. But as an organic ligand, thiol is an unstable surface adsorption agent under hydrothermal treatment. During coarsening, it can be destroyed and desorbed into water. So the pure OA stage in these systems reveals the rule of a relatively small size range, ceasing at the size of about double the volume of a primary particle.

Under more strong and stable surface adsorption, the pure OA stage may hold for a longer time and larger size. Concentrated NaOH shows its strong surface adsorption effect and even leads

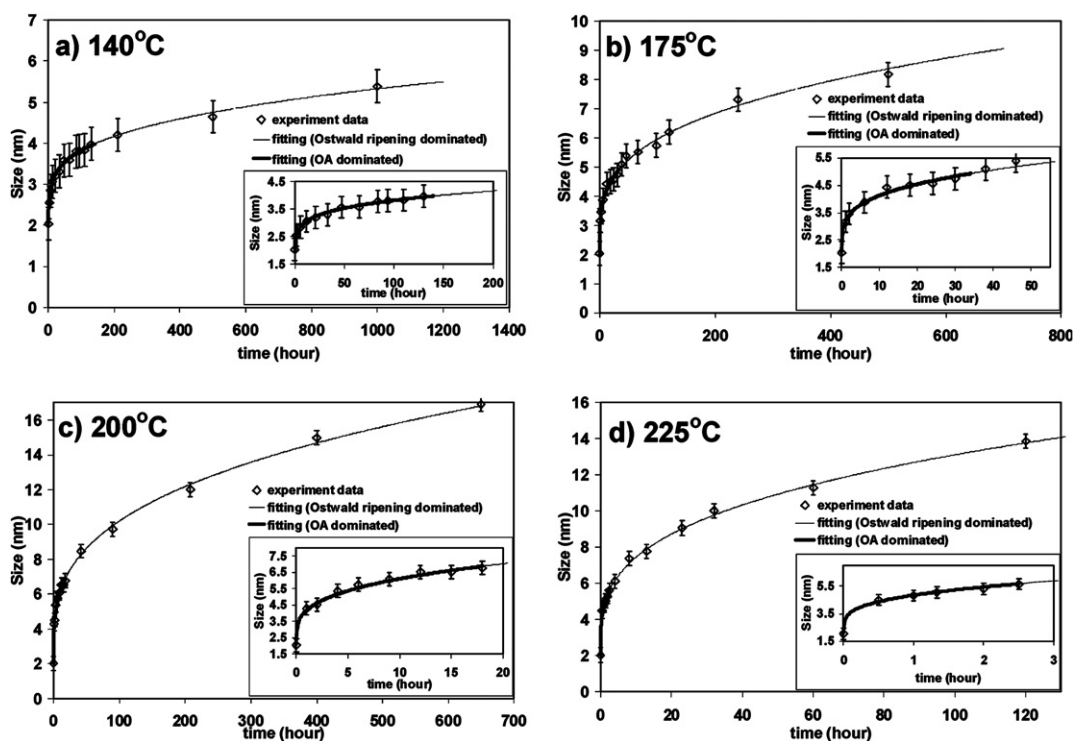


Fig. 6 Experimental data and fitting results for particles sizes vs. time at different temperatures. The whole growth process of ZnS nanoparticles in water is controlled by the (OA + OR) mechanism; inset are enlarged plots for the OA-dominated coarsening at the initial stage. Reproduced with permission from *J. Phys. Chem. B*, 2003, **107**, 10470. Copyright 2003 Am. Chem. Soc.

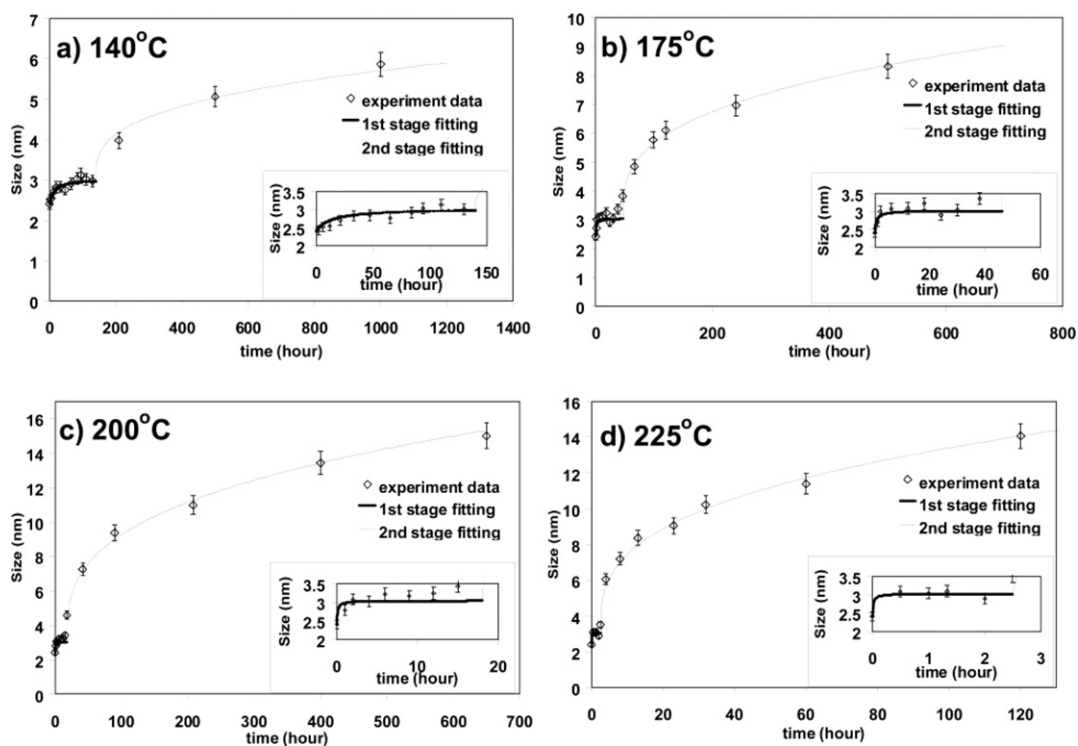


Fig. 7 Two-stage growth of mercaptoethanol-capped nano-ZnS in aqueous solution. In the first stage, the growth is controlled by the pure OA mechanism, as shown in enlarged insets. Reproduced with permission from *Nano Lett.*, 2003, **3**, 373. Copyright 2003 Am. Chem. Soc.

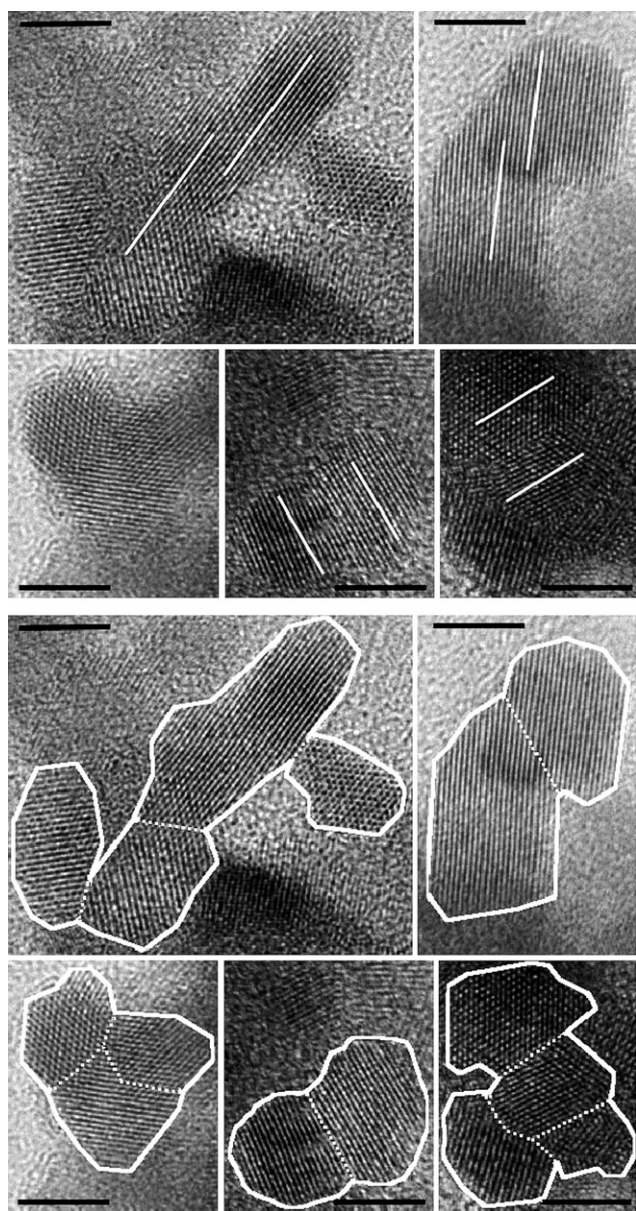


Fig. 8 Typical HRTEM images of the nanocrystal growth controlled by the OA mechanism in the thiol-PbS system. Larger crystals are constructed by smaller attached nanocrystals with size equal to primary particles (4–5 nm). The white parallel lines highlight the misorientation between two regions of the assembled particle. Schematic outlines of each image illustrate the attachment scheme of OA. Scale bars: 5 nm. Reproduced with permission from *J. Phys. Chem. B*, 2007, **111**, 1449. Copyright 2007 Am. Chem. Soc.

to the negative interfacial free energy.⁸ So, when ZnS nanoparticles are hydrothermally treated in 4 M NaOH solution,¹⁰⁵ the crystal growth, limited by the exclusive OA mechanism, occurs at a large size scale in the first stage and the primary particles grow into a size over hundred times the original volume (see Fig. 9).

Why does the effect of strong surface adsorption make the nanocrystal growth in the initial stage *via* the pure OA mechanism? Further investigation reveals that the effect can slow down the dissolution of particles in solution, so that the OR mechanism is thermodynamically prohibited in an unsaturated solution.

Thus, the OA mechanism will be the only growth mode during the initial growth and the time period is prolonged with the increase of surface adsorption. As shown in Fig. 10, the concentration of zinc ions in the supernatant of the ZnS-NaOH system was checked during coarsening. It needs a relatively long time before the solution reaches saturation and during the period, crystal growth is limited by the pure OA mechanism.¹⁰⁵ Comparing with Fig. 9a, it can be seen that the time point for saturation matches that of the pure OA growth ceasing.

Actually, research from Searson and coworkers also revealed that surface adsorption of anions (*i.e.* Br⁻, CH₃CO₂⁻, and ClO₄⁻) on the nanoparticles can slow down the OR growth rate.^{26,27} Combining with the above examples, it can be seen that to select strong and stable surface adsorption of inorganic ions will be the effective means to obtain the pure OA growth and keep it for a long time period.

3.2 OA-based crystal growth kinetic models

3.2.1 ($A_1 + A_1$) Model.

By introducing the strong surface adsorption, the pure OA-based growth can be obtained, which simplifies the nanocrystal growth process for the followed studies on growth kinetics. Inversely, OA-based growth kinetic modeling will provide critical information and understanding regarding the crystal growth mechanism.

Based on the characteristics of the OA mechanism, the first OA growth kinetic model was developed to fit the experimental growth curves (particle size *vs.* growth time).²³ As shown in Fig. 7, in the first stage of hydrothermal treatment mercaptoethanol-capped nano-ZnS, the primary particles quickly double in average volume. It meant that two primary particles attached and combined into a larger secondary particle according to the relation of volume between the primary particle and the second one.

A nanoparticle is tens to thousands of times larger than a small molecule but far smaller than a macroscopic crystallite. So it is possible that the growth of nanoparticles *via* OA may share some characteristics with the collision reactions of molecules from the point of view that both processes produce a whole entity right after the reaction.^{18,107} Under hydrothermal coarsening, the Brownian motion of nanoparticles are assumed to be drastic. When two adjacent primary particles collide, the coalescence may occur on the premise that these two particles share a common crystallographic orientation. Thus two primary particles attach to each other and combine into a secondary one. The OA kinetic model can be interpreted as the following “reaction”:



where A_1 is a primary nanoparticle, B is the product of the coalescence of two primary nanoparticles, and k_1 is a kinetic constant for the “reaction” between the two particles. So a growth model based on the above equation was deduced:

$$d = \frac{d_0(\sqrt[3]{2k_1t + 1})}{(k_1t + 1)} \quad (3)$$

where d_0 and d are the average size of primary particles and the average particle size at time t , respectively. As shown in Fig. 7, the results fitted by the kinetic model agreed well with the

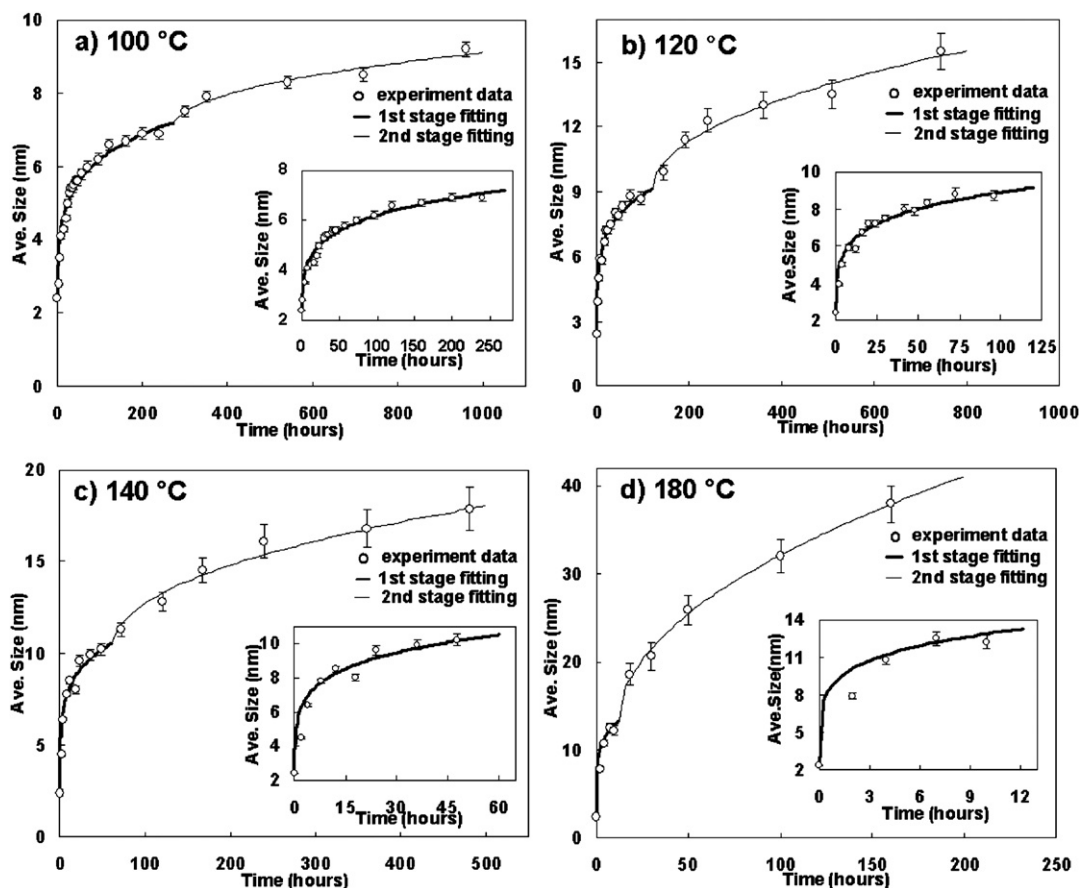


Fig. 9 Two-stage growth of ZnS nanocrystals in 4 M NaOH solution. In the first stage, the growth at a large size scale is controlled exclusively by the OA mechanism, as shown in enlarged insets. Reproduced with permission from *J. Am. Chem. Soc.*, 2006, **128**, 12981. Copyright 2006 Am. Chem. Soc.

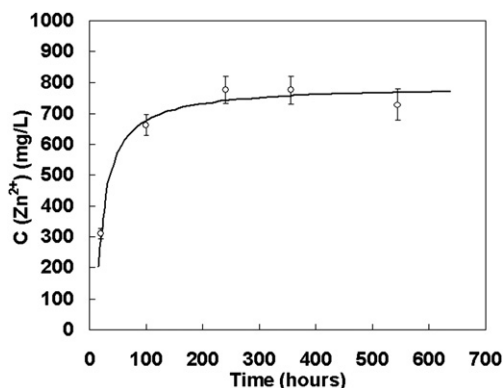


Fig. 10 The Zn^{2+} concentration in the supernatant of ZnS-NaOH system at 100 °C vs. coarsening time. Reproduced with permission from *J. Am. Chem. Soc.*, 2006, **128**, 12981. Copyright 2006 Am. Chem. Soc.

experimental data in the first stage, while the growth in the second stage can be fitted by the classical OR kinetic model.

On the basis of the above kinetic model, further studies were proceeded to gain a more thorough understanding of the growth behavior. Penn discussed the OA growth from the degree of the electrostatic interaction between particles in solution.¹⁹ The interactions such as electrostatic force and van der Waals are assumed as the main ingredients determining the kinetic rate constant. While Ribeiro *et al.* described the growth behavior of

nanoparticles by considering the diffusion and coagulation of colloids,²⁴ and drew a conclusion that the viscosity of the liquid medium played an important role in growth by the OA mechanism, which is governed by an inverse proportional relationship with respect to the rate constant. Their models presented more detailed physical meanings for the possible OA-growth pathway and for the OA-based growth rate.

However, the above model only discussed the “reaction” between the primary particles ($A_1 + A_1$). That is, only primary particles are assumed to combine into secondary particles, then the “reaction” will stop. So in the system, there only exists two kinds of nanoparticles: primary particles and secondary particles. In fact, the attachment between two other particles such as a primary particle and a secondary one, even a multilevel one also exists, and is often experimentally observed.^{19,23,102} So based on the experimental observation, a more sophisticated OA growth kinetic model was developed as follows.¹⁰⁴

3.2.2 ($A_1 + A_i$) Model. Still, the OA growth behaviors are taken as the collision and reaction of molecules. But here, the built model considers not only the OA of ($A_1 + A_1$) but also the OA of ($A_1 + A_i$). That is, the direct attachments also occur between a primary particle and a multilevel particle, such as ($A_1 + A_2$), ($A_1 + A_3$), *etc.*, but the coalescence between A_i and A_j ($i \geq 2, j \geq 2$) is neglected. Such consideration may be a more proper and general description of the OA growth kinetics of

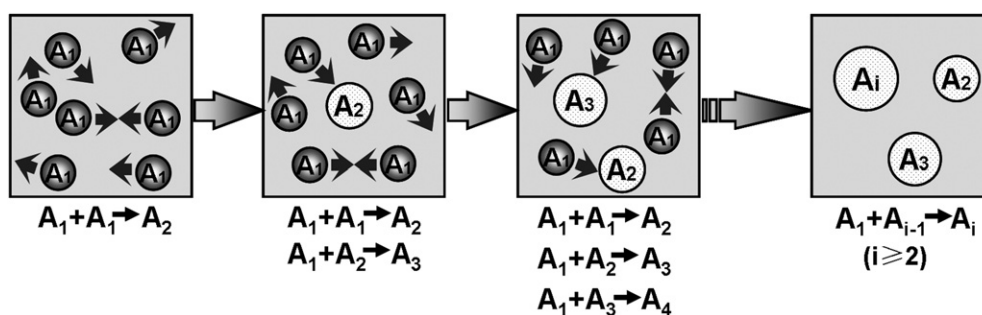
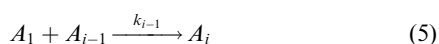


Fig. 11 Schematic graph illustrating the growth of nanocrystals by oriented attachment: two primary particles collide and coalesce in the same crystallographic orientation ($A_1 + A_1$). Then, a secondary particle comes into being. The attachments also occur between primary particle and multilevel particle, such as ($A_1 + A_2$), ($A_1 + A_3$), etc. But the attachment between A_i and A_j ($i \geq 2, j \geq 2$) is neglected. Reproduced with permission from *J. Phys. Chem. B*, 2007, **111**, 1449. Copyright 2007 Am. Chem. Soc.

nanocrystals capped with easily destroyed organic ligands. The ligand-capped primary particles act as the “active centers” to collide and attach other particles. As the multi-level particles are little and the surface agent on them is easier desorbed, it brings the low possibility of OA between multilevel particles and a relatively short OA dominant period. The process of OA-based growth in this way can be illustrated in Fig. 11.¹⁰⁴

The OA-based growth of nanoparticles can be analogous to the reaction between molecules, which is classically described by the Smoluchowski equation.²⁵ The Smoluchowski equation has been used universally in the fields of colloid chemistry, aerosol dynamics, and atmospheric science. But most of the research is focused on the theoretical prediction of the structure and properties of aggregation by using computer simulations, especially in fractal geometry.^{108–111} In recent years, the Smoluchowski equation has also been used to describe the aggregation of nanocrystals and coagulation of colloids in theory, and to predict the size distribution.^{112–115} But only a little work was done to fit the experimental data by the Smoluchowski theory, for both the complicated solution of the equation and the difficulty in controlling the experiments. Zhang and coworkers adopted the equation to fit the transformation kinetics of crystallization and growth in the solid phase of titania.¹⁰³ The fitting is greatly simplified by neglecting the influence of temperature and the concentration of particles on the OA-based growth for dry titania samples. As to the OA-based growth of nanoparticles in solution, these influence factors should be considered. The latter is closer to the essence described by the Smoluchowski equation.²⁵

The “addition model” of the Smoluchowski equation is a limiting case of aggregation.^{110,116} It involves monomer–monomer reactions and monomer–multimer reactions. The multimer–multimer reaction can be neglected. It has been found that the modified “addition model” of the Smoluchowski equation is suitable for describing the OA growth kinetics under easily destroyed surface adsorption, such as organic capping agents.¹⁰⁴ The monomers for OA under hydrothermal conditions are the primary nanoparticles. When the primary particles are exhausted, the crystal growth goes into the second stage. The growth *via* OA can be described as follows:



where A_1 is the primary nanoparticle, A_i is the particle containing i primary particles, and k_i is reaction rate constant. The hypotheses in the growth are: (a) the reaction between A_i and A_j ($i \geq 2, j \geq 2$) is neglected, because of their larger mass, immovability, and low probability of interaction, and (b) the reaction is irreversible. When the primary particles are exhausted, the reactions stop. That is, the crystal growth in this way finishes, which occurs at the end of the asymptotic growth kinetic curve.

So the time evolution of the concentration of A_1 and A_i are:

$$\frac{dN_1}{dt} = -2k_1 N_1^2 - N_1 \sum_{i=2}^{\infty} k_i N_i \quad (6)$$

$$\frac{dN_i}{dt} = k_{i-1} N_1 N_{i-1} - k_i N_1 N_i \quad (i \geq 2) \quad (7)$$

where N_1 and N_i are the concentration (number per unit volume) of primary particle, and the concentration of particle A_i ($i = 2, 3, 4, \dots$) after growth *via* OA for a period of time, t . The reaction rate constant k_i can be taken from the Smoluchowski theory.¹¹⁷ It is assumed that the diffusion coefficients for secondary particles, D_i ($i \geq 2$), are negligibly small compared with D_1 of the primary particles. So

$$k_i = 4\pi(R_1 + R_i)D_1 \quad (8)$$

where R_i is the radius of the particle containing i primary particles. According to the equivalent-volume relation, it can be given by:

$$R_i = i^{1/3} R_1 \quad (9)$$

R_1 is the radius of the primary particle.

For eqn (6)–(9), a numerical simulation is used to get the particle distribution at different times. Euler’s polygon method is introduced to the program and a first-order expression of Taylor’s formula is used as follows:¹¹⁸

$$N_{(i,t+\Delta t)} = N_{(i,t)} + \frac{\partial N_{(i,t)}}{\partial t} \Delta t \quad (10)$$

So the time step Δt in the calculation should be small enough to ensure the accuracy of result. Usually, $\Delta t = 1/(N \cdot D_1)$ is selected,¹⁰⁹ where N is the number of nanoparticles.

By this solution, the size distribution of particles can be obtained at a certain time. According to the definition of the volume-weighted average particle size,¹¹⁹ the average particle size, d_{eq} , which is consistent with the average particle size determined by XRD line broadening, can be expressed as:

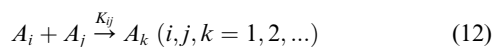
$$d_{eq} = \frac{\sum N_k d_k^4}{\sum N_k d_k^3} \quad (11)$$

where d_k is the size of particle containing k primary particles. Thus, the increasing particle size with time revolution will be calculated.

3.2.3 ($A_i + A_j$) Multistep kinetics model. When nanocrystalline ZnS coarsens in concentrated NaOH, as an inorganic agent, the surface adsorption of NaOH is stronger and relatively stable during coarsening. The newly formed coalescent multilevel nanoparticles are also immediately surrounded by the strong surface adsorbent. Thus the probability of OA between multilevel nanoparticles is also very high. Only the multistep OA growth between multilevel nanoparticles will lead to a pure OA growth stage at a large size scale (Fig. 9).

The multistep OA growth agrees with the Smoluchowski theory.¹⁰⁵ In the multistep OA kinetics model ($A_i + A_j$), the “reaction” of collision and coalescence may occur between any of two multilevel nanoparticles in the system. So, the collision and coalescence between particles here are unlimited and closer to the actual growth behaviors. As the size of the nanoparticle increases, the collision cross-section of the particle enlarges, while the motion rate of the particle decreases rapidly. Putting these two together produces an effect that with particle size increasing, OA-based growth slows down quickly and will finally stop. The process of growth in this way is illustrated in Fig. 12a and Fig. 12b and shows the typical HRTEM observation of crystal growth in this way.

The multistep OA-based growth kinetic model can be described as follows:



A_k is the particle which contains primary particles of number k , and $k = i + j$. So the time evolution of the concentration of A_k is:

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} N_i N_j - N_k \sum_j K_{kj} N_j \quad (13)$$

where N_k is the concentration (number per unit volume) of A_k (k -mers) and K_{ij} is the rate constants for the reaction between the particles (i -mers and j -mers). The terms in the right-hand of eqn (13) describe the formation and loss of the particles (k -mers), respectively. The hypotheses in the growth are (a) the reaction is an irreversible, random, and binary one between A_i and A_j , and (b) spatial fluctuations in particle density and particle shape are neglected.

The rate matrix K_{ij} is given by the Smoluchowski formula:²⁵

$$K_{ij} = 4\pi(R_i + R_j)(D_i + D_j) \quad (14)$$

where R_i and D_i are the radius and diffusion coefficient of the particle containing i primary particles.

The proposed model was also based on the modified Smoluchowski equation and by numerical simulation, the

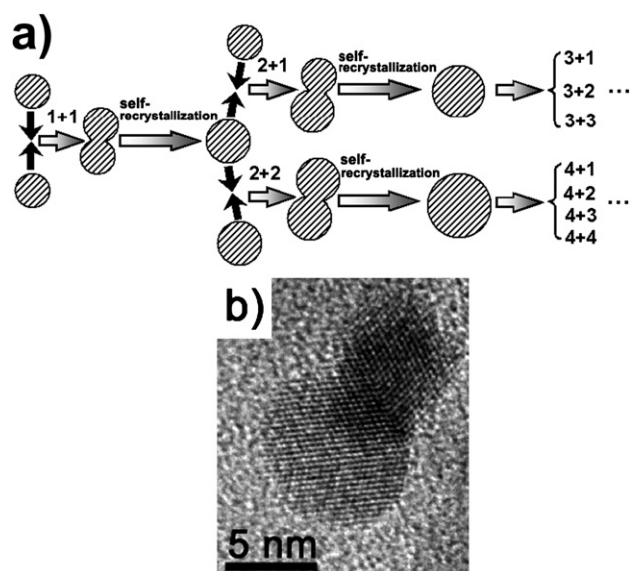


Fig. 12 (a) Scheme of the OA-based growth of nanoparticles: two primary particles collide like molecules, and coalesce in the case of the same crystallographic orientation (1 + 1). After self-recrystallization, a secondary particle comes into being. The same “reactions” will take place between two other particles, such as (2 + 1) and (2 + 2), and further multistep “reactions” occur. (b) HRTEM image showing two ZnS nanoparticles attached to each other in the common crystallographic orientation. Reproduced with permission from *J. Am. Chem. Soc.*, 2006, **128**, 12981. Copyright 2006 Am. Chem. Soc.

experimental data can be fitted with the built kinetic model (Fig. 9). Because all of the possible binary interactions between nanoparticles in the systems are considered, the OA kinetic model shows its generalization. But on the other hand, the complexity and calculation magnitude of numerical simulations are greatly amplified.

The series of kinetic models tends to be gradually closer to the realistic growth behavior controlled by the OA mechanism. To take OA-based nanocrystal growth as the collision and reaction between molecules reveals the characteristics of nanoparticles at the transition state of molecules and bulk materials. The “molecular-like” kinetic models provide the deep insight of the OA-based crystal growth and by fitting experimental data, meaningful physical parameters and rules can be obtained to understand the microscopic crystal growth process.

For example, the activation energy can be obtained by using the OA kinetic models to fit the experimental data. The activation energy is an important parameter determined by the process of step-controls. Due to the scarcity of data directly from experiments, systemic studies on the activation energy of the OA growth were hardly reported. By fitting the OA growth kinetics, we can get the apparent activation energy from the experimental data of growth rate, which can be used to further analyze the microscopic dynamic process of controlling the growth.¹⁰⁵

Another example is the effect of the OA mechanism in controlling the particle size distribution. In the chemical solution synthesis of nanocrystals, organic surfactants are broadly introduced to minimize the size distribution.¹²⁰ However, the achievements from kinetically control often largely rely on the

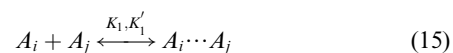
experience in experiments. The deficiency in fully understanding the inner mechanism will result in little effective approaches taken to control the synthesis in purpose. From the above growth kinetics, we know that strong surface adsorption (organic and inorganic) helps to generate the exclusive OA growth in the initial stage. During the OA growth, small particles diffuse fast due to their low mass. So, the smaller particles grow faster than the larger ones in the system, which facilitates a narrow size distribution. It has been reported that a “focusing” of size distribution was found during the nanocrystal growth in the CdSe-TOPO system and the InAs-TOP system.³⁶ The authors suggested that continuous monitoring and adjustment of the monomer concentration could reliably prepare larger amounts of uniform nanoparticles, especially when the growth approaches the equilibrium of the asymptotic curve. Obviously, the OA growth kinetics are the major factor that determines the size distribution and the variety of shapes for nanosynthesis *via* surface capping.

Until now, studies on the OA-based growth kinetic models mainly focused on the systems of nanoparticles (zero dimension nanoscale materials), and little on two- or three-dimensions. Ribeiro *et al.*¹²¹ adopted the classical stepwise polymerization model^{122–124} to discuss the formation of anisotropic nanoparticles (one-dimension) by the OA mechanism. The main problem in these systems is not the building and solving of mathematical models, but the physical interpretation related to the kinetic models, such as the kinetic driving force and controlling factors of primary particles assembling in a certain direction. Also, the branch occurring on the one-dimensional structures enlarges the difference between calculated results and experimental statistical data. In fact, a homogenous one-dimensional structure formed by the OA mechanism is scarcely reported, due to the difficulties of changing from isotropy to anisotropy.¹²⁵

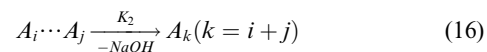
3.3 Further understanding of microscopic OA dynamics

3.3.1 Two-step reaction during the OA growth. Reasonable building of kinetic models can provide a possibility to understand the microscopic growth process *via* the OA mechanism, which is often not easy to observe directly. For the OA-based crystal growth, it often undergoes two reaction steps:^{19,24} one is the diffusion step of the nanocrystals (it can be regarded as “random walk” behavior of nanoparticles. The motion of nanoparticles in a fluid is due to Brownian motion and fluid convection, which is much slower than the diffusion of molecules); the other is the coalescence and desorption of surface species. And the obtained E_a represents the activation energy for the slowest step.

The OA undergoes two reaction steps: first, the nanocrystals (i -mers and j -mers) diffuse in the solution until collisions form a complex:



Second, there is an attachment by bonding in a proper orientation and a desorption of the surface species:



Thus the obtained E_a represents the activation energy for the slowest step.

For a ZnS system, a series of activation energies was obtained by fitting the experimental data of growth rate.¹⁰⁵ By comparing, it is concluded that under strong surface adsorption, the diffusion of nanocrystals is the slowest step for OA, though one can imagine that the strong adsorption also makes the disposal of surface ligands more difficult.

3.3.2 Particle rotation before coalescence. When two or more individual particles collide, they may have no common crystallographic orientation. In this case, the prerequisite that the primary nanoparticles be in compatible orientations does not apply. In order to achieve the structural accord at the interface, the primary particles would be free to rotate into an orientation. This process is directly related to the reduction of surface energy, aimed at minimizing the area of high energy faces. In this respect, the crystal growth *via* OA can be also named the grain-rotation-induced grain coalescence (GRIGC) mechanism,^{126,127} which is illustrated in Fig. 13. This process of attachment is followed by a process of rotation, which leads to a low-energy configuration, thereby forming a coherent grain–grain boundary and eliminating the common grain boundary, producing a single larger nanocrystal.

The grain rotation is likely induced by the thermal energy provided by the electron beam, which provides the opportunity to directly observe the OA dynamic process. For example, in the system of heterostructural SnO₂/TiO₂ nanoparticles,⁹³ after 1 min of electron irradiation, the nanoparticles began a spontaneous counterclockwise rotational motion. Finally, after 15 min, the particles undergo some diffusional motion, relaxing the surface and concluding the OA process. The whole process is illustrated in Fig. 14.

3.3.3 Self-recrystallization (self-integration) after coalescence. More often, we are not lucky enough to catch the moment when two individual particles just coalesce together, because in

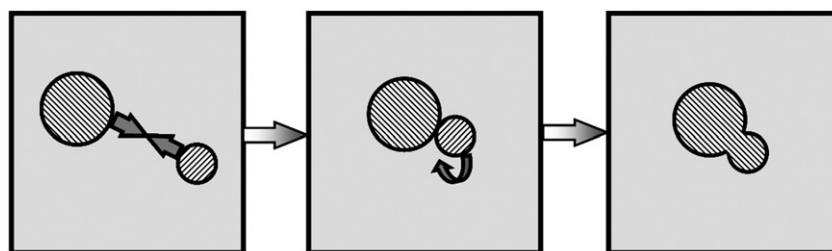


Fig. 13 Schematic of the particle rotation to get a structurally consistent nanocrystal during the process of OA.

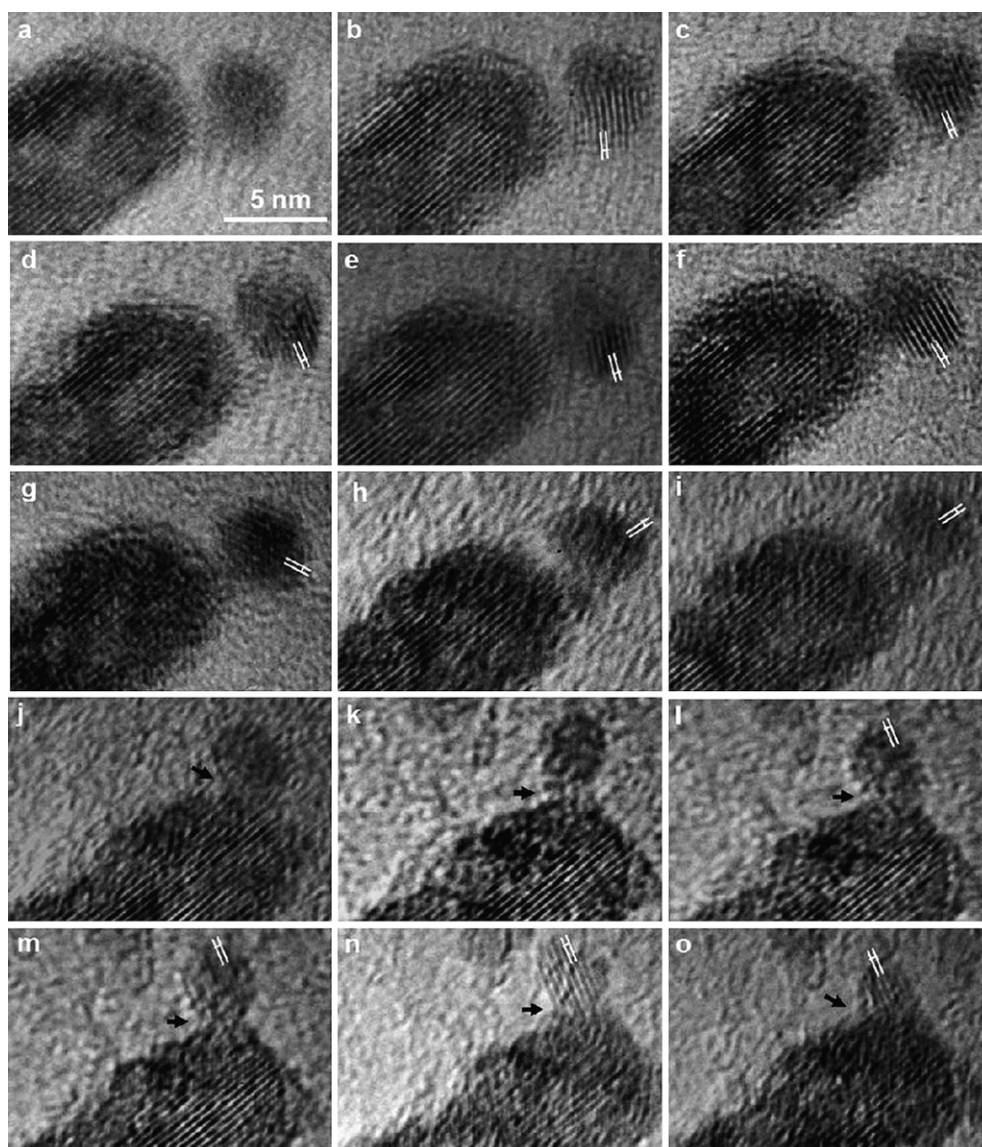


Fig. 14 Spontaneous orientation by rotation alignment of SnO₂ over TiO₂ tip. The white bars show SnO₂ planes and are a guide to the eyes in the rotation during the process of OA. Each image corresponds to a time interval of 1 min. Reproduced with permission from *Appl. Phys. Lett.*, 2007, **91**, 103105. Copyright 2007 Am. Institute of Phys.

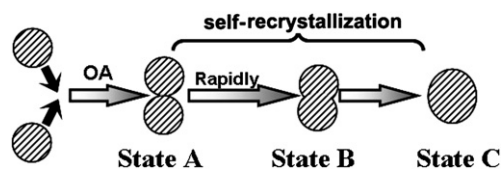


Fig. 15 Schematic of self-recrystallization after the particle coalescence by the OA mechanism.

view of energy, this state of newly produced particles is not stable and will undergo an adjustment of morphology named self-recrystallization.¹²⁸ When two particles just attached without self-recrystallization, the radius curvature at the joint is negative. According to the Gibbs–Thompson relation,

$$\mu = \frac{2\gamma\Omega}{R} \quad (17)$$

where μ is the chemical potential, γ is the surface free energy, Ω is volume per atom, and $1/R$ is the radius curvature, the chemical potential at the joint is negative. Thus atoms sited on other places are thermodynamically favored to move to the joint. As described in Fig. 15, it is proposed that the self-recrystallization should be as follows.

The oriented attached nanoparticle might undergo state A, state B, and state C. In experiments, though state A is formed *via* OA firstly, it is almost not observed in most systems by the TEM technique. Thus, it is supposed that the self-recrystallization from state A to state B is very rapid. But one can believe that the self-recrystallization from state B to state C might be slow, thus irregular small particle attachment geometries (state B) are captured frequently when the sizes of the assembling units are small. On the other hand, when the sizes of the assembling units become larger, the possibility of OA growth decreases, so there is enough time for nanoparticles to self-recrystallize into round shapes (state C).

The most recent development in studying the growth process of nanoparticles by the OA mechanism was by Zheng *et al.*,¹²⁹ where the first direct microscopic observation of OA dynamics was fulfilled by using TEM with a liquid cell. The recrystallization during the OA process is clearly observed and by this technology, we promisingly obtain more detailed and *in situ* information for the microscopic dynamics of OA-based growth.

Summary and outlook

This article summarizes the OA-based growth kinetics, especially the control over obtaining the pure OA mechanism under the strong surface adsorption and the progress of OA kinetic models. The effect of surface adsorption was demonstrated to impact more on the OR growth kinetics than on the OA growth process. The influence to the former can lead to thermodynamic prohibition, while to the latter, the adsorption/desorption only brings the kinetic limitation. It is interesting that the OA growth occurs by direct particle coalescence, regardless of the strong surface adsorption. Further exploration in this area will probably generate a general understanding of crystallization itself. The “molecular-like” OA growth models can provide the microscopic understanding of the OA growth process, taking the OA growth behaves as the collision and reaction between molecules. The proposed growth kinetics will be meaningful to the self-assembly strategies for materials including colloids, polymers, and even biologic species.

The OA mechanism has shown its increasing importance and role in self-assembly preparation. Kinetic modeling of crystal growth can provide critical information regarding the growth mechanism. To understand the microscopic process of nanocrystal growth by the OA mechanism can makes us utilize its positive roles in the preparation of nanostructural materials (*e.g.* the self-assembly of anisotropic crystals), and avoid its negative effects to properties (*e.g.* structural defects). Currently, the methods to produce controllable and uniform size and morphology are mainly based on the kinetic control. Besides the scientific significance, studies on the crystal growth kinetics are possible to generate effective methods to tailor and predict the properties of materials in the synthesis and growth. Just like that the effect of surface adsorption has been proved to greatly act on the nanocrystal growth. Other factors such as solvents, electric field, and magnetic field, are assumed to impact the nanocrystal growth behaviors and the corresponding products. By adjusting these effects, the crystal growth will possibly be controlled, which facilitates the further exploration of the OA-based growth kinetics.

The growth of nanocrystals is a rich field of research that needs progress in the theories and experiments. Further studies on the microscopic growth behaviors *via* the OA mechanism will help us to understand the crystallization process and control the development of structures. Exploitation of more powerful facilities may capture the real and *in situ* dynamic information. Alternatively, molecular simulation will provide the proper explanation on the molecular scale, as the OA-based growth process often fails to be directly observed, such as the adsorption and desorption of molecular, the collision mode and process, and bonding.

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