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A R T I C L E S

A Multistep Oriented Attachment Kinetics: Coarsening of ZnS Nanoparticle in Concentrated NaOH

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Abstract: Crystal growth of ZnS nanoparticles during hydrothermal coarsened in 4 M NaOH occurs via a two-stage process. In the first stage, the primary particles grow into a size over hundred times of the original volume. The initial growth rate can be fitted by an asymptotic curve. High-resolution transmission electron microscope (HRTEM) data indicate that in this stage, crystal growth mainly occurs via a multistep crystallographically specific oriented attachment (OA). The higher the coarsening temperature, the earlier the first stage ends. In the second stage, an abrupt transition from asymptotic to square parabola growth kinetics occurs. The crystal growth data can be fitted by a standard Ostwald ripening (OR) model consistent with growth controlled by dissolution/precipitation of ions in solution. HRTEM data indicate that a minor amount of OA-based growth also occurs in the early period of the second stage. A new multistep OA kinetics model analogous to the reaction between molecules was proposed to illustrate the asymptotic growth in the first stage of coarsening. The effect of concentrated NaOH was discussed and proved to be the key that hindered the OR process, attributing to the almost exclusive pure OA-based growth of ZnS particles in the first stage.

Introduction

Nanoscale semiconductor crystallites such as CdS, CdSe, and ZnS, have been investigated extensively for their unique size-dependent properties of optics, electricity, magnetism, and so on.[1,2] A fundamental investigation of quantum size effects requires the preparation of nanoscale materials with controllable size and morphology. Thus studies on the crystal growth kinetics as well as the microstructure development in nanoparticles play a critical role in controlling the size-dependent properties.[3-6] Early studies on the kinetic model for coarsening of bulk materials were based on the Ostwald ripening (OR) mechanism,[7-9] which involves the growth of larger particles at the expense of smaller ones, driven by a decrease of surface energy. The coarsening mechanism is often controlled by the diffusion of ions to the particle surface from solution. The growth kinetics in this way mainly depends on the properties of the materials, the characteristics of the solution, and the nature of the interface

between the crystals and the surrounding solution. Generally, all of the above contributing factors are independent of crystal size. Once the particle sizes reduce to nanoscale, this atom-by-atom model of crystal growth is not unique. For example, it revealed that irregular, even anisotropic morphologies, such as elongated crystal (chains), butterflies, and horseshoes, can be obtained in various synthesis methods.[10-14] The formation of these anisotropic morphologies can be explained by a new crystal growth mechanism named "oriented attachment (OA)", where two crystallographically oriented nanoparticles combined together to form a larger one,[15,16] leading the formation of nanoparticles with irregular shapes.

OA crystal growth phenomena have more often been observed for nanoparticles with relative small size and weight.[17,18] Also, the attachment between secondary particles, even larger ones, are observed.[18,19,21]Unfortunately, it was found during OA crystal growth, that the OR growth mechanism usually occurred simultaneously,[19] sometimes accompanied by phase transformation also.[20] All of these lead to difficulties for investigating this

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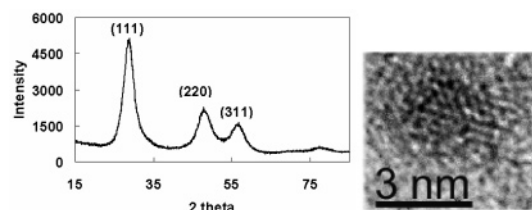(21) Penn, R. L. *J. Phys. Chem. B* **2004**, *108*, 12707.

Figure 1. XRD pattern (left) and HRTEM image (right) of the as-synthesized ZnS nanoparticle.

size dependent crystal growth mechanism, especially kinetically. Previously, the author has studied the OA growth kinetics during hydrothermal coarsening of mercaptoethanol-capped nanocrystalline ZnS, where OA crystal growth kinetics was found only between two primary particles.[18] Afterward, OA and OR mechanisms occur simultaneously, making it difficult to study the multistep OA kinetics at long range. In this work, by introducing concentrated NaOH to "arrest" the OR process, a multistep OA growth mechanism was observed. A new kinetics model describing OA mechanism was built for interpreting the growth behavior between secondary or larger nanoparticles.

Experimental Section

The primary ZnS nanoparticles were synthesized in aqueous solution without any surfactant. An aqueous solution of 0.1 M sodium sulfide was dropped into equimolar 0.1 M zinc chloride aqueous solution. The mixture was stirred vigorously to obtain a homogeneous reaction, aged for 30 min, and rinsed with distilled water several times until Cl⁻ was below detection by 0.1 M AgNO₃ solution. The precipitates were dried and ground into powder for the following kinetic experiments. All of the above experiments were processed at room temperature.

An amount of 0.15 g as-synthesized nanocrystalline ZnS and 10 mL of 4 M NaOH were mixed in a Teflon-lined stainless steel autoclave of 23 mL capacity. The autoclaves were sealed and heated at 100 °C, 120 °C, 140 °C, and 180 °C, separately. For time series experiments, autoclave containers were taken out and quenched to room temperature at the appropriate time interval. The precipitates were collected and washed with pure ethanol until the pH was ~7.0.

X-ray diffraction (XRD) was used to identify the crystal structures and average particle sizes of samples. Diffraction data were recorded using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (45 kV, 40 mA) in the continuous scanning mode. The 2θ scanning range was from 15° to 85° in steps of 0.03° with a collection time of 20 s per step. The average crystallite size was calculated from the peak broadening using the Scherrer equation.

High-resolution transmission electron microscopy (HRTEM) was used to confirm the particle size and to determine the particle morphology. Samples were prepared for HRTEM study by dispersing the ZnS powder onto 200-mesh carbon-coated copper grids. HRTEM analyses were performed using a JEOL JEM2010 HRTEM at 200 kV. Approximately 10 HRTEM images of nanoparticles in zone axis orientations were recorded from the samples to identify the microstructures.

To check the solubility of ZnS in 4 M NaOH under different coarsening times, the autoclave containers were taken out and quenched to room temperature; the clear supernatants was quickly extracted and further centrifuged once. This whole process was done within 4−5 min. After that, the content of zinc in the whole sample was detected by inductively coupled plasma (ICP) (Ultima2).

Results

The typical XRD pattern and HRTEM of as-synthesized ZnS are shown in Figure 1. XRD data reveal that the nanoparticles are mainly sphalerite, with calculated average size of ~2.4 nm

in [111], [220], and [311] directions. HRTEM observations confirm the size, morphology, and the phase structures from XRD.

ZnS nanoparticles coarsened at four different temperatures were characterized with the same methods as above. Figure 2, panels a, b, c, and d show the calculated sizes of nanoparticles versus coarsening time at 100 °C, 120 °C, 140 °C, and 180 °C, respectively. The figure shows that the growth of ZnS nanoparticles shares the same rule for these four temperatures. In each temperature, crystal growth can be divided into two stages. In the first stage, the growth of ZnS nanoparticles follows an asymptotic curve, suggesting the character of OA mechanism.[18,19,22] The ceasing time of this stage decreases as the temperature rises. The maximum size of nanoparticles in this stage approaches to 7.2, 9.1, 10.5, and 13.0 nm, for 100, 120, 140, and 180 °C, respectively. In the second stage, crystal growth fits the parabola, with a rate slower than in the initial stage, and the size of nanocrystalline increases continuously with time increases.

The growth kinetics in the second stage can be described and fitted by OR theory. The general kinetic equation for these cases can be written as[9,23]

$$d_{eq}{}^n - d_0''^n = K_2(t - t_0') \tag{1}$$

where d_{eq} is the mean particle size at the time t, while d_0' is the particle size at the starting time t_0' in the second stage. K_2 is a temperature-dependent material constant, and n is an exponent relevant to the coarsening mechanism. Table 1 shows the fitting results. With temperature increases, the values of d_0' increase, while t_0' decreases rapidly and n is almost equal. The fitted result shows that $n \approx 2$ is the best one, which means that the coarsening kinetics in the second stage is mainly controlled by precipitation/dissolution reactions at the particle/matrix interface.[7−9] Actually, as proposed,[18] though the crystal growth data of the second stage can be simply fitted by OR, that does not mean that the crystal growth in the second stage is via the pure OR process. OA and OR are proposed to coexist in this stage,[18,22] and since the large size of the particles gradually slows down the OA, the contribution of OA to the crystal growth can be negligible in the fitting.

Fitting of the crystal growth in the first stage by using eq 1 yielded a very large exponent of $n > 10$, which bears no physical meaning. Actually, HRTEM observation revealed that the OA mechanism was mainly observed in this stage. Figure 3 shows HRTEM images of ZnS particles in 4 M NaOH at 100 °C for 20 h. It can be seen that each particle is typically formed by two particles attaching together via a common crystallographic orientation. The grain edges of coalescence are illustrated clearly. Thus most of the produced particles are with irregular shapes and abrupt edges, exhibiting the particular character of crystal growth by OA mechanism. Moreover, though particles with different sizes are observed for this time point, the majority of the particles are around 5 nm, which agrees well with the calculated average size from XRD.

Figure 4 shows the HRTEM images of ZnS particles when the treatment time approaches the end of the initial growth curve (240 h at 100 °C). It reveals that a part of the particles shows

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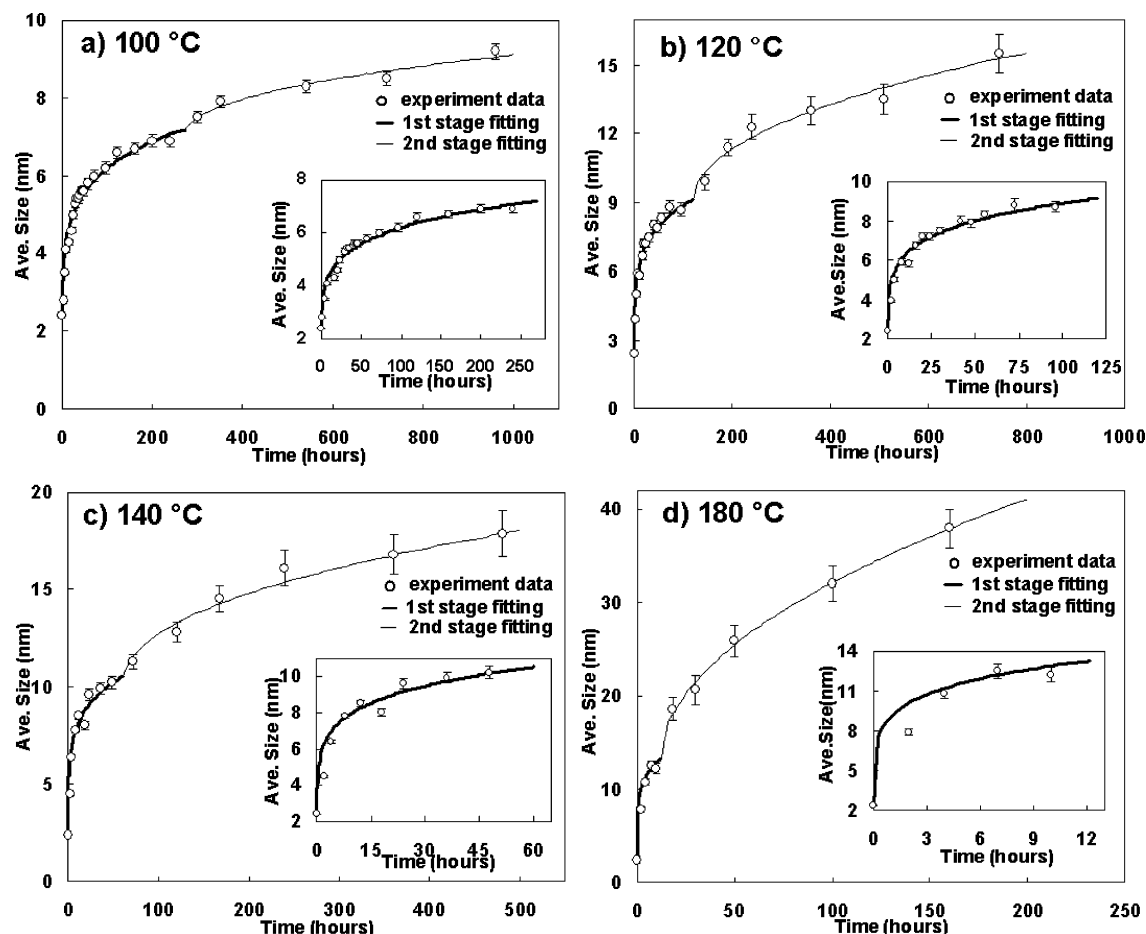(23) Joesten, R. L. *Rev. Mineral.* **1991**, *26*, 507.

Figure 2. Experimental data and fitting results showing the mean size vs time at each temperature; insets are enlarged plots for the first stage of growth.

Table 1. Estimated Values by Fitting the Experimental Data at Each Temperature

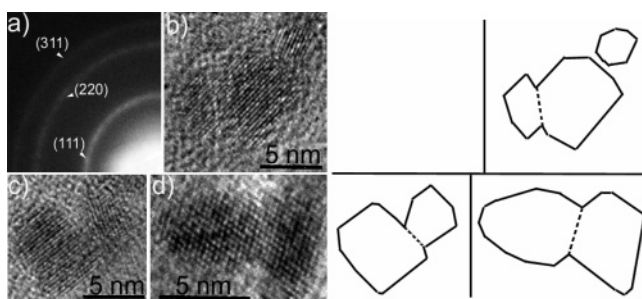|	for the first stage			for the second stage			
T (°C)	R_1 (nm)	K_1 ($= D_1 N_{1(0)}$)	a	t'_0 (hours)	d'_0 (nm)	K_2	n
100	1.2	7.5×10^3	−1.5	270	7.2	0.1076	2.216
120	1.2	8.0×10^4	−1.5	120	9.1	0.2841	2.077
140	1.2	4.0×10^5	−1.5	60	10.5	0.5189	2.221
180	1.2	9.1×10^6	−1.5	12	13.0	1.9784	1.975

Figure 3. Electron diffraction pattern (a) and typical HRTEM images (b−d) of ZnS nanoparticles hydrothermally treated in 4 M NaOH at 100 °C for 20 h. The right corresponding diagrams illustrate that two particles with the common crystallographic orientation attached into one.

Figure 4. Typical HRTEM images of samples hydrothermally treated in 4 M NaOH at 100 °C for 240 h. Growth by OA mechanism (a) and OR mechanism (b) can both be observed.

clear coalescence of two small "building blocks" (Figure 4a), while a part of the particles has smooth edges and round shapes (Figure 4b). The former preserves obvious characters of growth by OA mechanism, while the latter might be formed from crystal 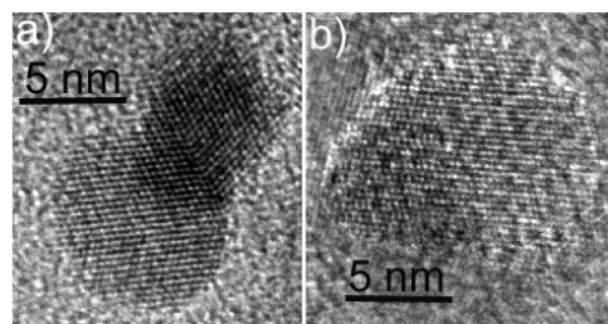growth by OR mechanism or might be the self-intergrated structure after OA growth. In a word, both the crystal growth characters of OA and OR mechanism coexisted at this critical point, while OA-based growth was still the dominant one. It was also found that the original 2.4 nm primary particles are almost being consumed completely in this time. The "building blocks" for OA growth are larger sized particles, indicating a multistep OA mechanism with primary, secondary, or larger nanoparticles as assembling units.

Figure 5 shows the state of the ZnS nanoparticles after being hydrothermally treated at 100 °C for 350 h. It reveals that most of the particles have a round shape and smooth edges; particles with irregular geometry are seldom found. This is consistent with the crystal growth characteristicss of OR and OA coexisting in this stage. In fact, considering that the initial particle radius of the second stage is given by the OA mechanism of the first
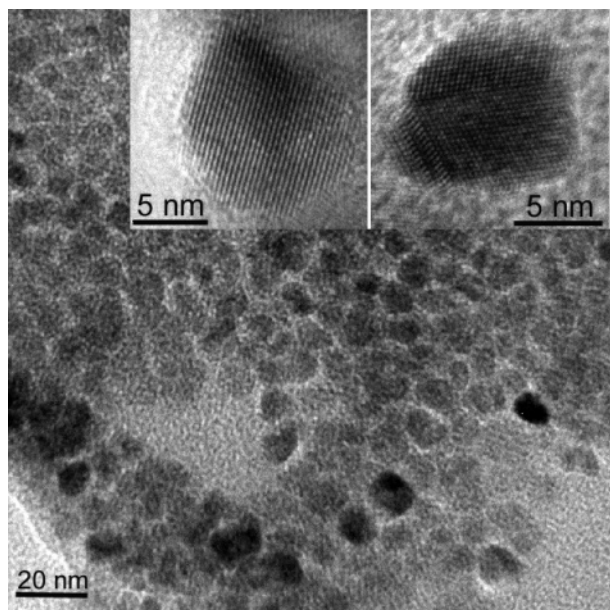
Figure 5. Typical TEM images of ZnS nanoparticles hydrothermally treated in 4 M NaOH at 100 °C for 350 h (inset, HRTEM images of coarsened particles). Most of particles coarsening by OR mechanism present a round shape with smooth edges. Inside of some particles, defects are the legacy of OA-based growth, as shown in the right HRTEM image of inset.

stage, we found the sizes of the particles are large enough that the OA is slowed down, and thus the actual contribution of OA in the second stage should be very little. Moreover, incorporated defects, such as twins and the layer defect are found in the round particles. Such incorporated defects normally came from OA-based growth in the earlier stage.[5,19] It reveals that such defects will be preserved during the self-intergration and OR process, since the transformation from twins and stack faults into pure sphalerite needs extra energy.[5]

Model of Multistep OA Kinetics. 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.[15,24] Under certain conditions (e.g., hydrothermal treatment), nanoparticles are assumed to act as the Brownian motion of molecules. 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. Since the sizes of the secondary particles are still very small, it is reasonable that they will continue to collide and coalesce. Thus the same "reaction" may go on and on between two multilevel nanoparticles in the system. 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 increases, OA-based growth slows down quickly. The process of growth in this way can be illustrated in Figure 6.

The OA-based growth of nanoparticles can be analogous to the reaction between molecules, which is classically described
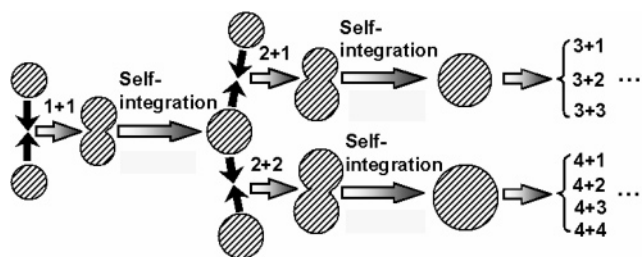

Figure 6. Scheme of the OA-based growth of nanoparticles: two primary particles collide like molecules, and coalesce in the case of the same crystallographic orientation (1 + 1). After self-integration, a secondary particle comes into being. The same "reactions" will take place between two other particles, such as (2 + 1) and (2 + 2), and further multistep "reactions" occur.

by the Smoluchowski equation.[25] The Smoluchowski equation has been used universally in the fields of colloid chemistry, aerosol dynamics, atmospheric science, and so on. But most of the researches are focused on the theoretical prediction of the structure and properties of aggregation by using computer simulations, especially in fractal geometry.[26-29] In recent years, the Smoluchowski equation has also been used to describe the aggregation (not coalesce) and coagulation of colloids observed in experiments and to predict the size distribution.[30] Zhang et al. adopted the equation to fit the transformation kinetics of crystallization and growth in the solid phase of titania.[20] 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.[20] 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]

Here, a modified model of Smoluchowski equation was used to analyze our experimental result, and the growth "reaction" can be described as follows:

$$A_i + A_j \xrightarrow{K_{ij}} A_k \quad (i, j, k = 1, 2, ...) \tag{2}$$
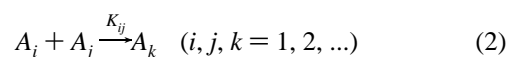
A_k is the particle which contains primary particles of number k, and $k = i + j$. So the time evolution of the concentration of A_k is

$$dN_k/dt = \frac{1}{2}\sum_{i+j=k} K_{ij}N_iN_j - N_k\sum_j K_{kj}N_j \tag{3}$$

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 eq 3 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.

Therefore, the rate matrix K_{ij} is given by the Smoluchowski's formula[25]

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

where R_i and D_i are the radius and diffusion coefficient of the particle containing i primary particles. According to the equivalent-volume relation between particles, we have

$$R_i = i^{1/3}R_1 \tag{5}$$

Here R_1 is the radius of the primary particle (1.2 nm for ZnS). In general, the particle diffusion coefficient, D_i, depends on their size and/or shape. It is assumed that D_i can be given by[27]

$$D_i = D_1 i^{\alpha} \tag{6}$$

where D_1 is the diffusion coefficient of the primary particle, and α is a constant.

Then the effective reaction rate constants for the aggregation of particles, K_{ij}, can be changed into

$$K_{ij} = 4\pi R_1 D_1 (i^{1/3} + j^{1/3})(i^{\alpha} + j^{\alpha}) \tag{7}$$

For eq 3, a numerical simulation is used to calculate the particles 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:[31]

$$N_{(i,t+\Delta t)} = N_{(i,t)} + \frac{\partial N_{(i,t)}}{\partial t}\Delta t \tag{8}$$

So the time step Δt in the calculation should be small enough to ensure the accuracy of result. Usually, $\Delta t = 1/(ND_{max})$ is selected,[27] where N is the number of nanoparticles, and D_{max} is the maximum diffusion coefficient of any of the nanoparticles in the system. Here we take $\Delta t = 1$ s, which has been tested as small enough to ensure the accuracy for the fitting.

All possible binary interactions among nanoparticles in the systems can be covered by a half-square matrix with $k \times k$. For ensure that the interaction over k is neglectable, k should be assigned a large enough value. All of the attachment between i-mers and j-mers can be enumerated as follows:

$$
\begin{bmatrix}
(1+1) & (1+2) & (1+3) & (1+4) & & \cdots & & (1+k) \\
 & (2+2) & (2+3) & (2+4) & & \cdots & & (2+k) \\
 & & (3+3) & (3+4) & & \cdots & & (3+k) \\
\cdots & & & & & & & \\
 & & & & (i+i) & \cdots & & (i+k) \\
\cdots & & & & & & & \\
 & & & & & & ((k-1)+(k-1)) & ((k-1)+k) \\
 & & & & & & & (k+k)
\end{bmatrix}
\tag{9}
$$

By simulation, a reasonable number for k is determined as 300, 550, 800, and 1100 for temperature of 100 °C, 120 °C, 140 C, and 180 °C, respectively. The k assigned over these values has no influence on the fitting results.

The parameter $(D_1 N_{1(0)})$ and constant α are two adjustable factors, where $N_{1(0)}$ is the concentration of A_1 at $t = 0$. The product, $(D_1 N_{1(0)})$, is an integral factor that controls the growth rate, while α determines the maximum of particle size (maximum of asymptotic curves). These two factors are independent

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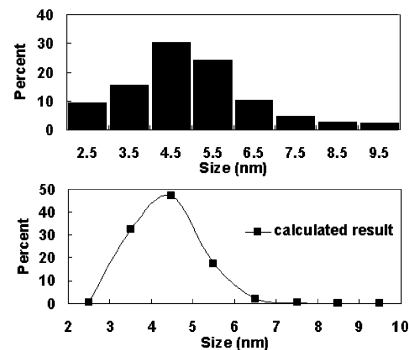

Figure 7. Particle size distribution of ZnS nanoparticles hydrothermally treated in 4 M NaOH at 100 °C for 20 h: (a) count from TEM images; (b) calculated result.

of each other. So by fitting the experiment data, $(D_1 N_{1(0)})$ and α can be estimated and obtained separately (Table 1).

The size distribution of particles at a certain moment can also be obtained via a calculation. Furthermore, according to the definition of the volume-weighted average particle size,[32] the average particle size at this certain moment, d_{eq}, which is consistent with the average particle size determined by XRD line broadening, can be expressed as

$$d_{eq} = \sum N_k d_k^4 / \sum N_k d_k^3 \tag{10}$$

where d_k is the size of particle containing k primary particles.

By using $R_1 = 1.2$ nm, the numerical calculation results are shown in Figure 2 as thick solid curves. It reveals that the increases of the particle size with time revolution are fitted well with those by experiments. Figure 7 shows the comparison of calculated size distribution with TEM experimental result. It reveals that the calculated size distribution is roughly consistent with TEM observation, while TEM statistics exhibit a wider size distribution, and the proportion of larger and smaller particles are higher than calculated results. The reason might be that in calculation, the size of the primary particle is set exactly as 2.4 nm with zero size distribution, whereas in experiment, the primary particles have a broad size distribution around 2.4 nm ($R_1 = 1.2$ nm), thus the TEM statistic is broader than the calculated one.

The kinetic constants vary with temperature and can be described by the Arrhenius equation

$$\log K = -\frac{E_a}{RT} + A_0 \tag{11}$$

where E_a is the apparent activation energy, A_0 is the preexponential factor, R is the universal gas constant, and T is the absolute temperature. Figure 8 shows the Arrhenius plot of kinetic constants K_1 and K_2. Here we take $K_1 = N_{1(0)}D_1$ as the apparent kinetic constant of OA, for $(D_1 N_{1(0)})$ is an integral factor and α is a constant independent of temperature. From the Arrhenius plot of various kinetic constants, we obtained the apparent activation energy of OA, $E_a(K_1) = 54.5 \pm 5.2$ kJ/mol, and the apparent activation energy of OR, $E_a(K_2) = 22.4 \pm 3.2$ kJ/mol.

Discussion

Under general conditions, OA and OR crystal growth mechanisms occur simultaneously.[19] It is found that the capping

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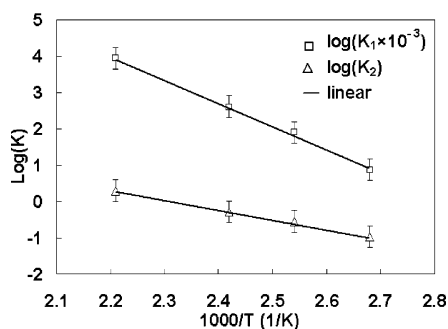
Figure 8. Arrhenius plot of the two kinetic constants.

Figure 9. ICP result showing the solubility of ZnS in 4 M NaOH at 100 °C vs time.

of mercaptoethanol on ZnS particles[18] was able to hinder the OR growth in the initial period of time, allowing the observation of an exclusive OA crystal growth mechanism between two primary particles.[18] Such a pure OA kinetics does not extend to secondary nanoparticles, possibly because the surface adsorption can be destroyed very easily under hydrothermal condition. Actually, research from another group also revealed that surface adsorption can slow down the growth rate of OR.[33] All of these indicate that it is possible for us to achieve multistep OA via an adjustment of the surface adsorption.

Influence of Surface Adsorption to OR Mechanism. OR can be limited by volume diffusion (diffusion of ions or atoms in the liquid solution or solid matrix), diffusion along the matrix grain boundary, or precipitation/dissolution reactions at the particle/matrix interfaces.[6] As described by eq 1, for $n = 2$, the coarsening kinetics is inferred to be limited by precipitation/dissolution reactions at the particle/matrix interface,[23] for $n = 3, 4, 5$, the coarsening kinetics is limited by processes related to diffusion.[6,18−19] As we can see, only the dissolution/precipitation step is closely related to the interfacial states of the particle/matrix, and thus can be adjusted via surface adsorption. The author previously found that OR growth of ZnS nanoparticles in water is controlled by the diffusion of ions ($n \approx 3$).[19] In this study, we chose the concentrated NaOH as an alternative hydrothermal solution by considering the following: (1) Our recent work shows high concentrate NaOH to have a very strong surface adsorption effect on ZnS that can even change the effective interfacial free energy into a negative value.[34] (2) The surface adsorption effect of NaOH on ZnS is very stable under hydrothermal conditions.[34] Different from that in water, we found the OR growth of ZnS nanoparticles in 4 M NaOH is controlled by the dissolution/precipitation at the interface ($n \approx 2$). This result indicates the dissolution/precipitation step of the OR mechanism has been slowed down by strong surface adsorption of NaOH.

The Effects of NaOH. As discussed above, concentrated NaOH was introduced as a strong adsorbent to ZnS nanoparticles. We found there are two effects of NaOH in this system. First, the solubility of ZnS in the concentrated NaOH solution is increased greatly. Second, the dissolution speed of ZnS nanoparticle is slowed down by the strong surface adsorption.

To verify this, we checked the concentration of zinc ions in 4 M NaOH at 100 °C against hydrothermal time. As shown in Figure 9, the concentration of zinc ions in the supernatant
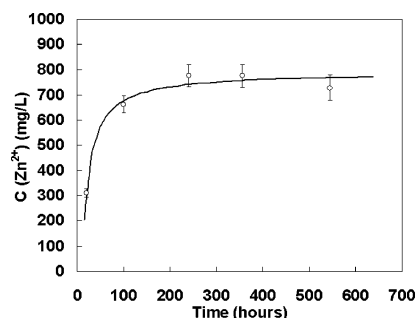
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increased gradually until the hydrothermal time reached 250 h. After that, the concentration of zinc ions in the solution are stable. This result reveals that the time period for ZnS to reach saturation (also dissolution/precipitation equilibrium) is about 250 h. In other words, the coarsening of ZnS is processed in an unsaturated solution for a long time period. Moreover, we found the time point for ZnS to reach saturation is consistent with the transition point from pure multistep OA to OR + OA (around 240−270 h), indicating the onset of OR is related to the saturated condition of the solution.

The Effects of Unsaturated Condition to OR and OA. As we know, in a solution far from saturated, the dissolution of solid is dominant, thus both large and small particles tend to dissolve thermodynamically. The OR process, in which the larger particles grow at the expense of the dissolution of smaller ones (driven by decrease in surface energy), is not favored in an unsaturated solution. So in the first stage the solid does not arrive at dissolution equilibrium; OR basically does not occur. On the other hand, oriented attachment of nanoparticles is not related to the dissolution-precipitation process. Thus the OA process will not be prohibited by the unsaturated conditions. As discussed above, we believe the adsorbent on the surfaces of the nanoparticles may affect the interfacial reaction of both OA and OR, although this is not comparable to the influence from the unsaturated condition, which determines whether or not the OR process thermodynamically occurs.

The Chemistry Possibly Occurred on the Nanoparticle Surfaces. From the microscopic viewpoint, the ZnS nanoparticle is a noncentrosymmetrical crystal. The $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}1)$, and $(11\bar{1})$ planes terminated with a S^{2-} layer, whereas opposite (111), $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, and $(\bar{1}\bar{1}1)$ planes terminated with a Zn^{2+} layer. We proposed that in strong NaOH solution, the opposite planes of crystal will absorb different ions, that is, S^{2-} terminated face adsorbed with Na^+, while Zn^{2+} terminated face adsorbed with OH^-. For one single nanoparticle, the total surface charge is near neutral. As we know, OA of ZnS is the coalescence of the Zn face of one nanoparticle to the S face of another nanoparticle; the electrostatic attractive effect of the adsorbed layers with opposite charges may not suppress but promote the OA. During OA, the surface adsorbed species (Na^+ and OH^-) must be excluded, but it is still very hard to investigate when and how the surface species is removed. From the analysis of E_a (see later), we can only conclude that the desorption of the surface species is not the rate-limiting step.

Physical Interpretation of the Activation Energy of the OA Process. As proposed by Penn[21] and Leite,[22] the OA undergoes two reaction steps: first, the nanocrystals (*i*-mers and

j-mers) diffuse in the the solution until collisions form a complex:

$$A_i + A_j \overset{K_1, K_1'}{\leftrightarrow} A_i \cdots A_j \tag{12}$$
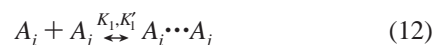
Second, there is an attachment by bonding in proper orientation and a desorption of the surface species:

$$A_i \cdots A_j \xrightarrow[-\text{NaOH}]{K_2} A_k \qquad (k = i + j) \tag{13}$$
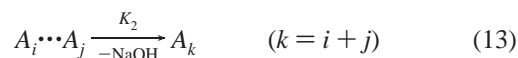
Thus the obtained E_a represents the activation energy for the slowest step.

For ZnS system, we have a series experimental data for comparison: (1) $E_a = 125.0$ kJ/mol for as-synthesized ZnS coarsened in water,[19] (2) $E_a = 136.8$ kJ/mol for mercaptoethanol-capped ZnS coarsened in water,[18] (3) $E_a = 54.5$ kJ/mol for ZnS coarsened in 4 M NaOH, and (4) $E_a = 53.0$ kJ/mol for ZnS coarsened in 8 M NaOH (paper under preparation). Since NaOH is a super strong surface adsorbing species,[34] more energy is needed for desorbing NaOH from the ZnS surface than what is needed for H_2O. In contrast, the E_a of ZnS coarsened in water is much higher than in NaOH. This indicates the desorption of the surface species is not the slowest step for OA. Moreover, we found the E_a of as-synthesized ZnS coarsened in water is almost the same as the E_a of mercaptoethanol-capped ZnS

coarsened in water; also, the E_a of ZnS coarsened in 4 M NaOH is almost the same as ZnS coarsened in 8 M NaOH. In conclusion E_a is dependent more on the diffusion media (water or NaOH solution) than on the capped species. In other words, we proposed that it is the diffusion of the nanoparticles in specific solution that determine the E_a.

Conclusion

We report that by hydrothermal growth of ZnS nanoparticles under 4 M NaOH, an exclusive multistep OA mechanism is observed. A new kinetics model based on the Smoluchowski equation (reaction between molecules) was built to describe the OA between nanoparticles. The calculated result agreed well with that by experiment. The observation of exclusive multistep OA mechanism is possible due to two factors: strong surface adsorption on the ZnS surface slows down the OR growth rate; the unsaturated condition of the solution prohibits the OR process thermodynamically.