

Oriented Attachment: An Effective Mechanism in the Formation of Anisotropic Nanocrystals

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In this article, we report the formation of dispersed anisotropic nanostructures by the oriented attachment mechanism, under hydrothermal conditions and in a system that all other growth processes are improbable. The comparison of dilute and agglomerated experimental conditions indicate that oriented attachment is an effective mechanism for the formation of anisotropic nanocrystals, and the conclusions can be extended to other nanometric systems.

Introduction

Solution-based procedures for the preparation of nanostructures (a “bottoms-up” approach) are considered very promising because of their potential to allow for precise control over the morphology of nanomaterials and, hence, over their properties.^{1–3} Anisotropic nanostructures such as nanowires and nanorods are of great interest, since the quantum confinement effects on these systems are also shape-dependent. Thus, semiconductor nanorods are expected to offer improvements in the performance of solar cell devices, gas sensors, catalysts, and so on.^{4,5} In this article, we report the formation of dispersed anisotropic nanostructures, by the oriented attachment (OA) mechanism, under an experimental condition that inhibited all other growth processes. Although no ligands or surfactants were added to promote the attachment of the nanoparticles, the results indicate that OA is an effective mechanism for the formation of anisotropic nanocrystals.

The normal solution-based approach toward anisotropic nanomaterials has been applied successfully to various II–VI and III–V semiconductor (e.g., CdS, CdSe^{6–8}) and oxide systems (e.g., TiO₂⁹). Anisotropy is attained by controlling the kinetics of the growth processes that follow nucleation. Particle coarsening (i.e., Ostwald ripening) is a common process in several nanomaterials. This mechanism is based on reactions of particle dissolution and ion reprecipitation, due to the size dependence of crystal solubility, which is described by the Thompson–Freundlich equation.¹⁰ Growth by coarsening usually produces nearly spherical morphologies, which are thermodynamically more stable because of the minimization of the overall surface energy. Peng et al.⁶ stated that the addition of high monomer concentrations in solution prevents coarsening by inhibiting particle dissolution and enables a supersaturation state in solution. Hence, surface deposition of monomers over energetic crystal facets results in a kinetically driven anisotropic growth of nanostructures.

Other approaches for the preparation of anisotropic nanocrystals by solution-based routes without the addition of high monomer concentrations are reported in the literature. Tang et al.¹¹ gave a very interesting example of the assembly of “building blocks” for the formation of CdTe nanowires. The

authors ascribe the spontaneous assembly of nanoparticles to dipole–dipole interactions. Polleux et al.¹² produced anisotropic TiO₂ nanocrystals by a ligand-directed assembly of nanoparticles. The anisotropy was attained by increasing the ligand content, and the authors ascribed the growth behavior to the oriented attachment mechanism.^{13,14} Cheng et al.¹⁵ reported a procedure for the large-scale synthesis of SnO₂ nanorods by a solution-based chemical method. Vayssieres and Graetzel¹⁶ described the preparation of SnO₂ nanorod arrays by a controlled aqueous growth. The authors affirmed that the synthesized nanorods appear to be composed of smaller particles assembled in an oriented manner. However, the above-mentioned investigations relating to the formation of SnO₂ nanorods have not addressed the anisotropic growth mechanisms directly.

The OA mechanism has recently been found to be a significant mechanism in the growth of several nanomaterials.^{17–22} This process seems very promising as a route for the preparation of complex-shaped nanostructures using nanoparticles as “building blocks”. Several papers have discussed the role of OA in the anisotropic growth of nanocrystals, including Tang’s aforementioned work. However, little has been done to clarify the mechanism in the synthesis of nanoparticles. A recent paper by Cho and coauthors²³ discusses the OA process as the main mechanism involved in the construction of anisotropic PbSe nanocrystals in several shapes. The authors used Tang’s proposition—the alignment of preformed nanoparticles by dipole–dipole interactions—as the mechanism responsible for the anisotropy associated with the attachment. The process was observed concomitantly to the synthesis of the nanocrystals. A similar experiment was proposed by Yu et al.²⁴ for the synthesis of ZnS. The authors suggested that the formation of ZnS nanorods occurred through the oriented attachment of spherical nanoparticles formed in a precursor solution to preformed nanorods in solution. An interesting feature was the subsequent coarsening (Ostwald ripening) of the final nanorods, “smoothing” the nanoribbon surface.

The mechanism of anisotropic alignment of nanoparticles is still under discussion. It has been suggested that oriented attachments may occur by (i) collisions of aligned nanocrystals in suspension or (ii) rotation of misaligned nanoparticles in contact toward low-energy interface configurations.^{21,22} According to these suppositions, the anisotropic alignment is

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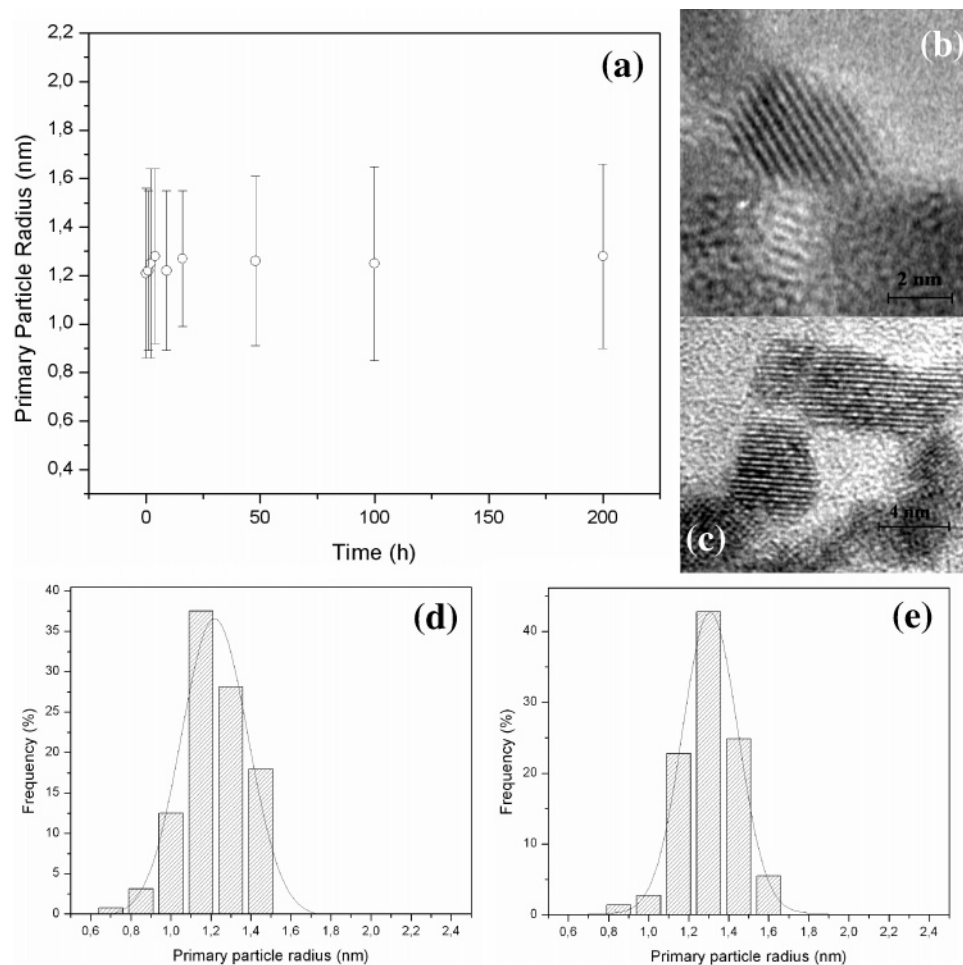


Figure 1. (a) Mean radius of primary particles as a function of hydrothermal treatment time; (b) HRTEM image of primary particles; (c) HRTEM image of coalesced particles; (d) primary particle size distributions for hydrothermally annealed SnO_2 suspensions at 200 °C for 2 h; (e) primary particle size distributions for hydrothermally annealed SnO_2 suspensions at 200 °C for 16 h.

attained by restricting the attachment process in some crystallographic directions. In this paper, we will show experimental results supporting the notion that the OA mechanism is the dominant process in the formation of anisotropic structures for nanomaterials. To demonstrate this, an experiment in which nanoparticle growth is induced by hydrothermal treatments was designed using preformed nanoparticles. Effects that may affect particle growth were minimized, and reactional mechanisms (such as monomer deposition) are absent. For instance, no ligands, surfactants, or monomers were added. Moreover, tin oxide is an ideal material for this kind of investigation, since its water solubility is extremely low, and hence, coarsening processes should be insignificant.

Experimental Procedure

The synthesis of tin oxide nanoparticles such as those used here is described in greater detail elsewhere.²⁰ This route is based on the hydrolysis reaction of tin chloride (II) dissolved in ethanolic alcohol at room temperature, forming crystalline nanoparticles at room temperature. To minimize external effects on the growth behavior, no surfactants were used in the preparation of the nanocrystals. Also, the chloride ions were cleansed by dialysis. The final synthesis product consisted of stable colloidal suspensions of nearly spherical SnO_2 nanoparticles in water, with a mean particle radius of approximately 1.2 nm and a suspension pH of 8.5. Part of the as-prepared suspensions was subjected to hydrothermal treatments at 200

°C for several periods of time in order to study the nanoparticle growth kinetics. It is important to note that growth by ion/monomer deposition does not occur in this stage, since all the reactions have already taken place.

In a second set of experiments, the as-prepared suspensions were coagulated by adding nitric and acetic acids (in two separated experiments) until the region of the isoelectric point (i.e., pH of approximately 3) was reached.²¹ These samples were also subjected to hydrothermal annealing for 24 h at 200 °C, to observe the effect of the agglomeration state on the growth of the nanocrystals. The evolution of nanoparticle morphology and size with increasing periods of hydrothermal treatments was analyzed by transmission electron microscopy (TEM; Philips CM200, operating at 200 kV).

Results and Discussion

The kinetics of the coarsening process was investigated by measuring the size of primary nanoparticles in the hydrothermally annealed samples prepared from the noncoagulated suspensions. Primary particles are considered spherical particles that have probably not undergone oriented attachment events, and therefore, any growth event would occur only by Ostwald ripening. Figure 1a shows the mean radius of primary particles as a function of hydrothermal treatment time. The high-resolution transmission electron microscopy (HRTEM) images in Figure 1b,c illustrate a morphological distinction between primary and coalesced particles. The mean particle radius was

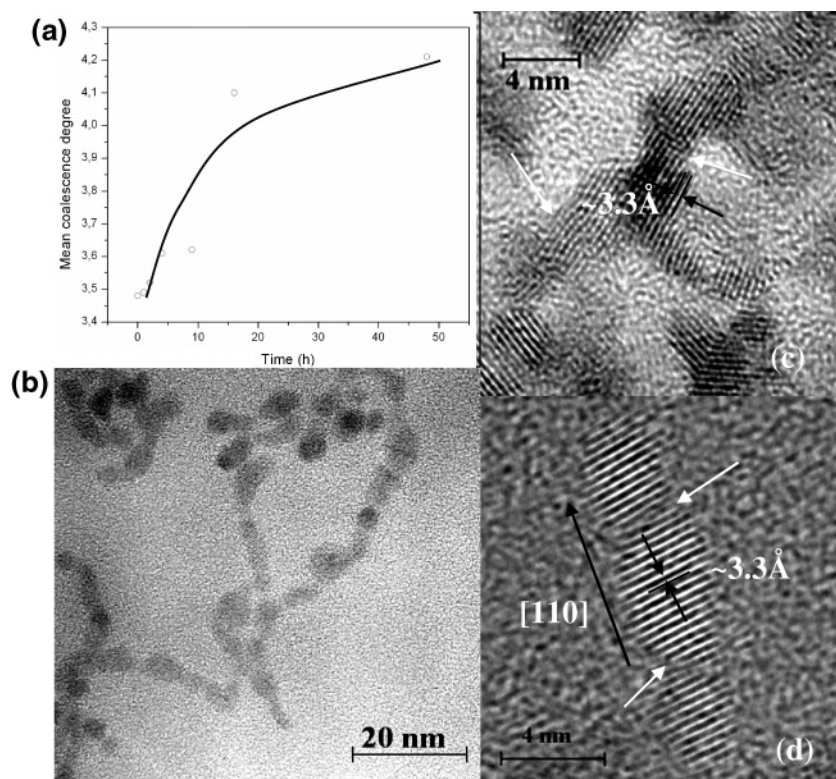


Figure 2. (a) Evolution of the mean degree of coalescence as a function of hydrothermal treatment time in samples prepared from noncoagulated suspensions; (b) HRTEM low-magnification image of a sample annealed at 200 °C for 48 h (noncoagulated suspension); (c) HRTEM image of irregularly shaped particles; (d) HRTEM image of anisotropic particles. The samples shown in parts c and d were also annealed at 200 °C for 48 h (noncoagulated suspension).

estimated on the basis of the measurement of at least 300 particles in the HRTEM images and by fitting a Gaussian function to the resulting distribution. The bars at the experimental points represent the distribution widths. Figure 1d,e illustrates primary particle size distributions for hydrothermally annealed SnO₂ suspensions at 200 °C for 2 and 16 h. The evolution of the primary particle size clearly shows that no significant growth occurred. This indicates that Ostwald ripening is not an important mechanism for tin oxide systems, as expected by the low solubility of this oxide. Hence, it can be expected that particle growth occurs only by a coalescence mechanism, i.e., oriented attachment.

The HRTEM characterization shows that hydrothermal treatments lead to particle coalescence. By considering that the degree of coalescence is defined as the number of particles that form a coalesced nanoparticle, it is possible to observe some aspects of the growth behavior of dispersed tin oxide particles using this approach, since the degree of coalescence relates to the length of the anisotropic nanocrystal. Figure 2a shows the evolution of the mean degree of coalescence as a function of the hydrothermal treatment time in samples prepared from noncoagulated suspensions. It can be observed that longer periods of hydrothermal annealing lead to higher degrees of coalescence, due to an increased number of coalescence events. Jun et al.⁹ suggested that the growth of anisotropic nanoparticles by OA should follow linear or exponential growth; however, such behavior is not observed. In fact, the best fit for the time dependence of the evolution of the mean degree of coalescence indicates a dependence of the type $y = c \cdot x / (1 + c \cdot x)$, where c is a constant. This behavior was discussed in detail by Ribeiro et al.²² and is consistent with the models proposed by Zhang and Banfield.^{18,19}

Figure 2b depicts a general TEM image of a sample annealed at 200 °C for 48 h, showing nanoparticles with both elongated

and sphere-like morphologies. In general, all the samples displayed primary nanoparticles and two other types of morphologies: irregular-shaped particles and anisotropic nanoparticles (Figure 2c and d, respectively). A HRTEM image of a SnO₂ nanorod is shown in Figure 2d. It is very important to note that the growth of this nanorod occurs in the [110] direction. This is another strong indication that growth occurred by neither monomer deposition nor coarsening, since (110) planes are the most thermodynamically stable. Hence, growth in the [110] direction is highly unfavored.²⁵ Growths in the [001], [010], and [100] directions were also observed in other elongated particles, indicating the statistical growth in attachment by effective collisions. It is also interesting to note that the nanorods display some dislocations in the regions where coalescence took place (white arrows).

Ribeiro et al.²¹ demonstrated that the coagulation of dispersed tin oxide nanoparticles by the reduction of the suspension pH up to the isoelectric point induces an increase in the mean particle radius, probably due to oriented attachment growth. The authors also concluded that growth by particle coalescence as a result of realignments of particles in contact is much more effective than oriented collision-induced attachments. This can be explained by the fact that, in the former case, there is a strong driving force for particle rotation, which tends to realign nanoparticles toward configurations of minimum energy, whereas in the latter, coalescence becomes a statistical process which depends on effective collisions. Moldovan et al.²⁶ described the driving force for particle rotation as a net torque resulting from the misalignment of neighboring particles. In this work, the hydrothermally annealed coagulated samples with nitric acid presented larger particles than those of noncoagulated samples, indicating the presence of the rotation process associated with agglomerates, where the growth behavior may be similar to that observed in two solids in contact. Figure 3a shows a HRTEM

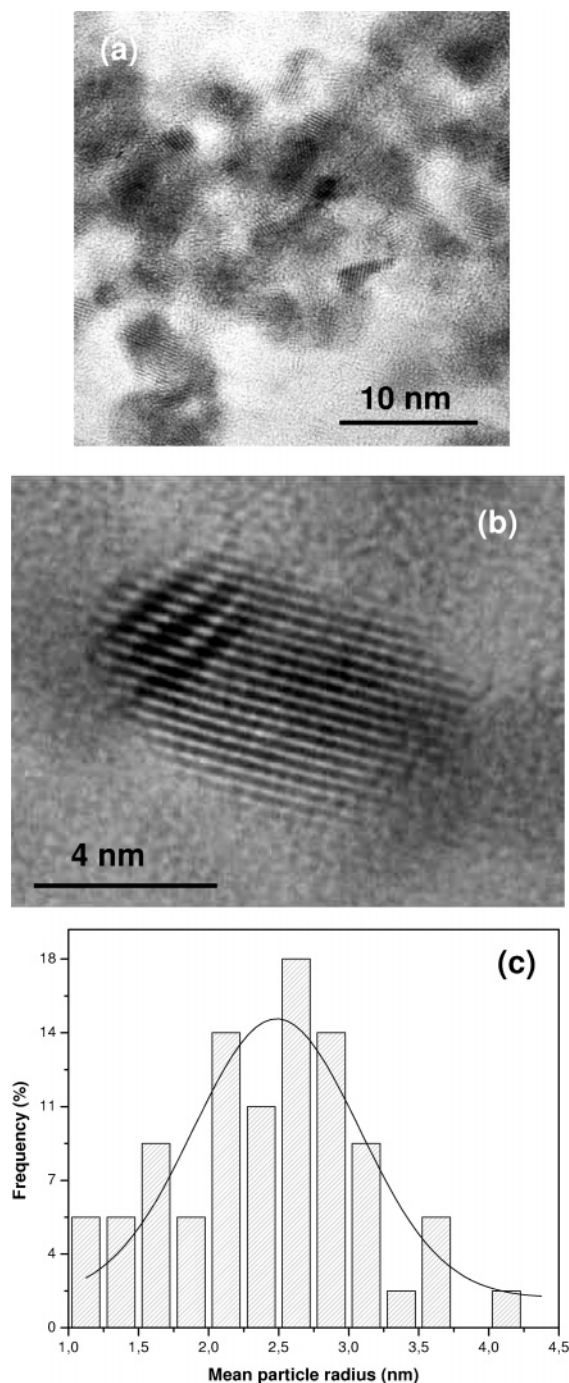


Figure 3. (a) HRTEM image of nitric acid coagulated sample treated hydrothermally at 200 °C for 48 h; (b) detailed image (HRTEM) of coagulated sample; (c) mean particle radius distribution.

image of a coagulated sample treated hydrothermally. Note the presence of nanoparticles with sphere-like morphologies and a few particles with elongated morphology. Figure 3b shows a HRTEM image of an annealed nanoparticle, revealing that the typical morphology of the nanocrystal grew by the oriented attachment mechanism. Although coalescence induced by particle rotation should lead to a set of low-energy configurations, we were unable to produce preferential anisotropic growth in the coagulated samples because agglomeration occurs randomly. This fact is confirmed by the histogram in Figure 3c, which plots the particle radius (assuming the radius of equivalent spheres) of the measured particles—from these data, it can be observed that growth occurred, but that resulting particles were

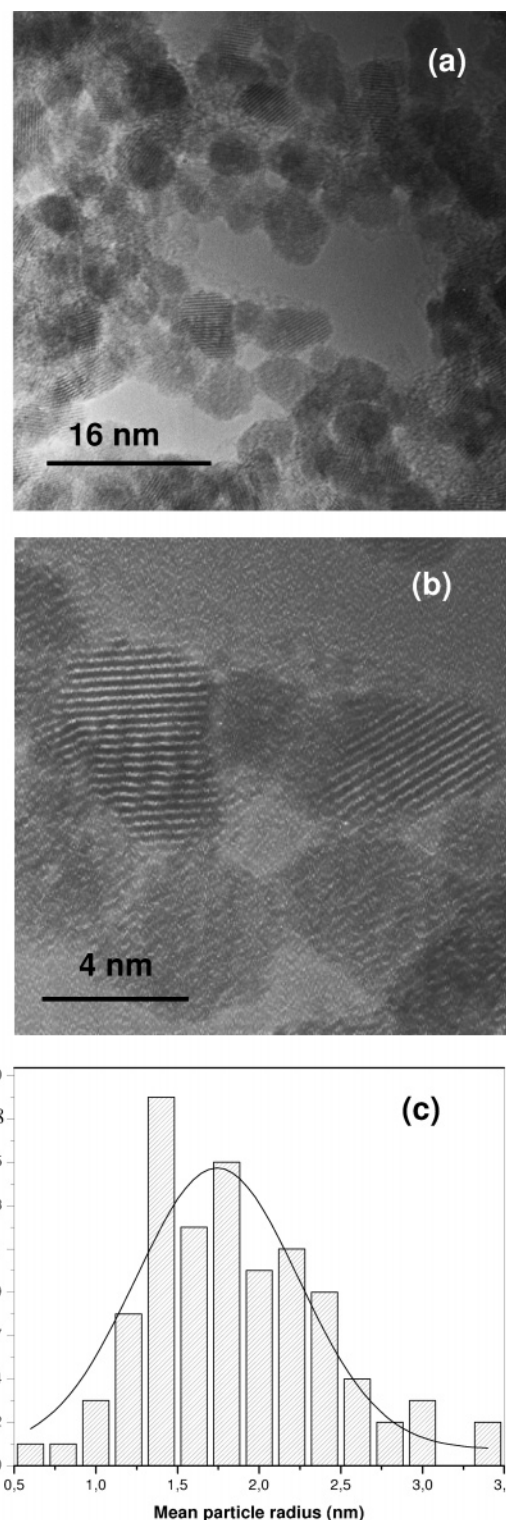
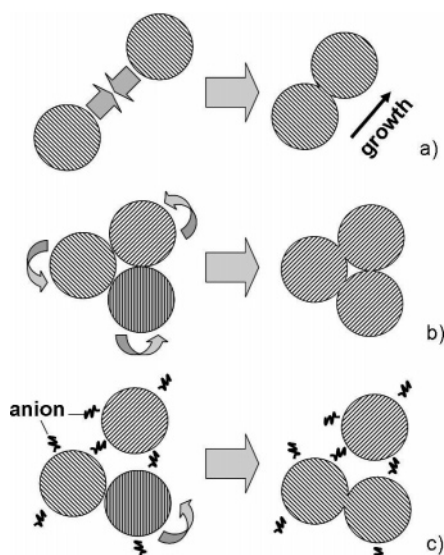


Figure 4. (a) HRTEM image of acetic acid coagulated sample treated hydrothermally at 200 °C for 48 h; (b) detailed image (HRTEM) of coagulated sample; (c) mean particle radius distribution.

not highly anisotropic (as seen in Figure 3a), indicating disordered growth.

However, a comparison of the behavior displayed by hydrothermally treated samples acidified with acetic acid, a short-chain organic acid, reveals a suppression of growth. Under the same conditions imposed on nitric acid acidified samples, this sample presented a particle distribution radius similar to that observed in the as-prepared suspension, as shown in Figure 4a and in detail in Figure 4b. The HRTEM image in Figure 4a

SCHEME 1:



(a) Coalescence in a well-dispersed system: the event is caused by an effective collision, and the growth direction is determined statistically. (b) Coalescence in an agglomerated system: the event can occur at any point of the particles' surfaces provided the crystallographic conditions are favorable. (c) Coalescence in an agglomerated system with dispersed organic anions acting as steric agents: the event depends on the contact between particles.

shows several spherical particles, suggesting that the short-chain anion dispersed in the medium interferes, imposing a steric effect between particles. This steric effect is a physical obstacle to oriented attachment and probably similar to the effect developed by surfactants, as has been reported in several papers.^{11,12,23} It is important to note that agglomeration also takes place in this condition, but the particle–particle contact is not effective. This assumption is confirmed by the mean particle radius distribution (Figure 4c).

The main hypothesis about the role of oriented attachment in hydrothermal conditions is summarized in Scheme 1, below. Under dispersed conditions, the anisotropic particles are formed by successive collisions without grain rotation. Here, the anisotropic growth is statistical and can lead to various particle shapes (Scheme 1a). Under agglomerated conditions, alignment by grain rotation can occur if the particles are in contact. However, since the crystallographic alignment can be satisfied at any point of the particles' surfaces, the final particle can result from several attachment events along the same surface, giving an uncontrollable shape (Scheme 1b). If the agglomerating agent (i.e., an acid, in the conditions discussed here) can cause a significant steric effect, as in the case of organic acids, the growth is hindered by the reduction of the Brownian motion—affecting the effective collision mechanism—and by the suppression of particle–particle contacts—affecting the driving force for rotation, i.e., the net torque resulting from the interfacial energies (Scheme 1c). These hypotheses lead to the use of selective surfactants, i.e., compounds having a high affinity with some crystallographic planes of the nanoparticle. This alternative can be effective under both agglomerated and dispersed conditions: in agglomerates, the presence of an adhered compound may lead to oriented agglomerates and, under dispersed conditions, the steric hindrance may lead to effective collisions in only one crystallographic direction.

Conclusion

In summary, the experiments described here demonstrated that the oriented attachment mechanism is an effective way to produce anisotropic nanostructures, where nanoparticles truly act as “building blocks”. By using an experimental setup in which external factors were minimized, it was possible to conclude that uncontrolled OA growth (e.g., by random agglomeration) does not lead solely to the formation of anisotropic nanocrystals. However, it seems that the anisotropic growth may be controlled by selecting surfactants (or strongly adsorbent species) which are adsorbed preferentially in specific planes. Moreover, it is possible to ascribe the predominant growth mechanism to oriented collisions between particles in the noncoagulated samples, and to coalescence induced by particle rotation in the coagulated samples. Hence, we believe that anisotropy may be obtained predominantly by controlling parameters, such as agglomeration and oriented collisions between particles.

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