

Formation Mechanisms of Uniform Colloid Particles*

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RECEIVED JANUARY 24, 2007; ACCEPTED FEBRUARY 8, 2007

Keywords
aggregation mechanism
colloid shape
partcles structures
precipitation

The relationship of the shape and structure of uniform colloidal particles to different mechanisms of formation by precipitation in homogeneous solutions is reviewed. Specifically, conditions leading to (a) amorphous spheres, (b) nonspherical crystals of different shapes, and (c) polycrystalline particles of different morphologies including spheres are distinguished. The last case is observed when larger particles are formed by aggregation of nanosized precursors. It is now recognized that the latter process is more common than previously understood. A model explaining the size selection of monodispersed spheres by aggregation is illustrated in the case of silver particles. It was also demonstrated that uniform polycrystalline particles of other shapes are generated by the aggregation process. Challenges faced in the effort to develop at least a semi-quantitative explanation of the shape factor in the latter case are outlined.

INTRODUCTION

The importance of particles uniformity is due to the fact that many of their properties depend on the size and shape. This aspect of finely dispersed matter was first uncovered more than a century and a half ago by Michael Faraday, who recognized that the red and blue color of colloidal gold dispersions was due to different particle size.¹ Despite the importance of Faraday's findings, during the next century the interest in such investigations remained rather low and only a few »monodispersed« colloids were described in the literature, mostly discovered by serendipity. The situation changed dramatically in the last fifty years as systematic research in this area was triggered by extensive evidence of the essential role played by finely dispersed matter in the environment and in numerous applications, especially in advanced technology. In particular, the advances in the latter case were prompted by the increased sophistication of new products requir-

ing high reproducibility or, more recently, by the progressive miniaturization of devices in microelectronics, medicine, *etc.*

Although various techniques have been used to prepare well defined colloids, the precipitation in homogeneous solutions remains the method of choice. Indeed, this approach offers more opportunities than any other for obtaining uniform particles, adjusting their properties by varying the experimental conditions, and scaling up the processes for mass production. As a result, numerous monodispersed particles of simple or composite natures in modal sizes ranging from several nanometers to several micrometers, and of different shapes have been described in the literature.²

Despite the progress in producing well defined dispersions, much less is known about the mechanisms of their formation, which may vary from system to system. In considering the generation of particles in solutions

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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one must pay attention to the chemical, as well as the physical aspects of the processes involved; while the two are interrelated, either one may dominate under certain conditions. For example, when polyvalent cations are involved, their propensity to form different hydrolyzed complexes (which can also include some anions) controls the chemical and morphological properties of precipitated particles. The situation is further aggravated by the sensitivity of such solutes to small variations in concentrations of reactants, temperature, *etc.* A good example of such effects can be found in the formation of different uniform alunites.³

From the physical point of view, the ideas on the conditions leading to particle uniformity have recently significantly changed due to new evidence obtained with improved instrumentation, such as high resolution electron microscopy. For a long time the mechanism proposed by LaMer was generally accepted, because it appeared simple and reasonable. In principle, it was assumed that monodispersed particles will form if a rapid burst of nuclei in the reaction solution is followed by their uniform growth, due to attachment of constituent solutes in a kinetically controlled manner.⁴ Figure 1 describes schematically the essential stages in the precipitation of solids in solutions. To produce uniform particles the LaMer process follows the left-hand side of the scheme.

Some years ago, however, experimental observations were made which contradicted the LaMer model. Figure 2 shows the transmission electron micrograph of uniform ZnS spheres obtained by decomposition of thioacetamide in a solution of zinc nitrate.⁵ The surprising finding was that the X-ray diffraction pattern had all the characteristics of the mineral sphalerite. Obviously, because of their shape these particles could not be single crystals and, indeed, it was shown that they were aggregates of uniform nanosize subunits. Similarly, spherical

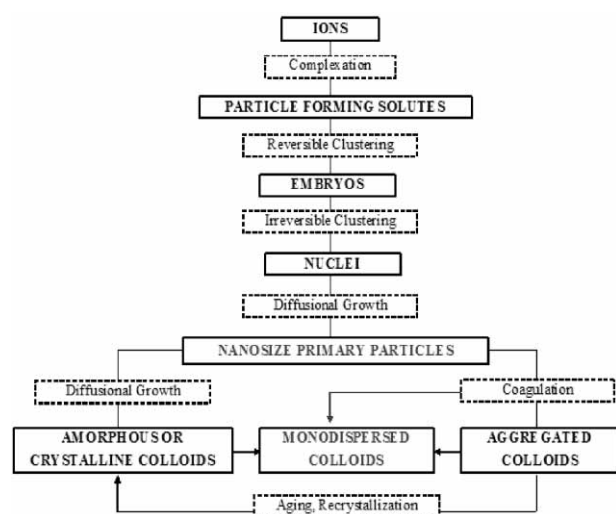


Figure 1. Stages in the formation of monodispersed colloids by precipitation in homogeneous solutions.

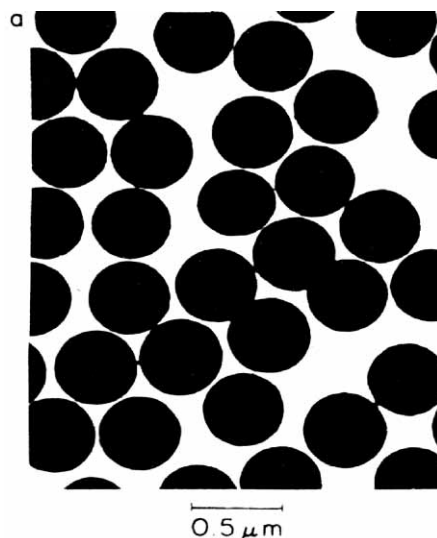


Figure 2. Transmission electron micrograph of uniform ZnS spherical particles obtained by decomposing thioacetamide in a solution of zinc nitrate.⁵

colloidal CdS particles prepared by homogeneous precipitation exhibited the characteristic X-ray pattern of greenockite.^{6,7} While at first it may have appeared metal sulfides to be unique in this respect, later on it was established that many uniform spherical colloids, including SnO₂,⁸ Fe₃O₄,⁹ BaTiO₃,¹⁰ Fe₂O₃,¹¹ Au,¹² and many others, were built of small precursors, yet had X-ray diffractograms of known crystalline materials. Furthermore, particles of other shape (ellipsoids, cubes, rods, platelets, *etc.*), which could have been easily mistaken for single crystals, were also proven to consist of much smaller subunits.^{13–15}

Thus, there is ample evidence now available confirming that a large number, if not the majority, of monodispersed colloids is formed by aggregation of nanosize precursors. This reaction path is given by the right-hand side of the scheme in Figure 1. In this case, the sequence of events leading to the nanosize stage is the same as in the LaMer model, but then these subunits aggregate rather than continue to grow.

In addition to particles which show crystalline or polycrystalline structure, there are numerous examples of uniform amorphous spheres, such as aluminum and chromium hydroxides, silica, mixed hydrous oxides, and others.¹⁶ These particles tend to form as a result of the hydrolysis of polyvalent cations, especially at moderately elevated temperatures. The resulting solute complexes then polymerize by condensation of the hydroxide ligands.¹⁶ The entire process was termed »forced hydrolysis«.

A schematic presentation of different mechanisms that may lead to the formation of monodispersed particles is given in Figure 3. Accordingly, *amorphous spheres* can be expected when solute species polymerize either di-

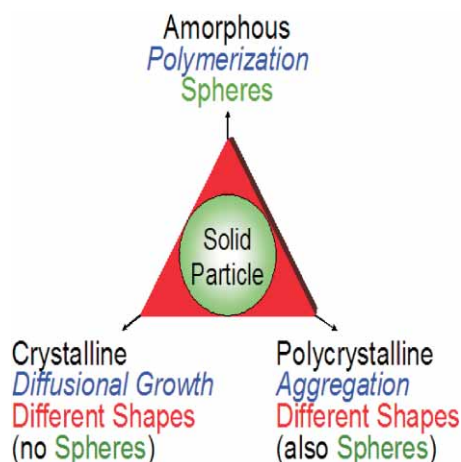


Figure 3. Schematic diagram of possible formation mechanisms of monodispersed uniform colloids in homogeneous solutions.

rectly, such as by forming polynuclear complexes, or by incorporating anions (*e.g.* sulfate or phosphate), which may facilitate or enhance the polymerization of solutes. Once the concentration of the latter exceeds their solubility, precipitated solids may, under suitably controlled kinetics, appear as uniform dispersions. As a rule, these processes never yield directly particles of any other shape but spherical (top of the triangle, Figure 3). Thus, in this case one deals with specific chemical reactions in solutions, which require a detailed elucidation in each case.¹⁶

The precipitation processes in which the nuclei grow to nanometer size by diffusion of constituent solute species and continue to do so to colloidal or larger crystals (perfect or imperfect) will result in *crystalline particles of different shapes, but never spheres* (left side at the bottom of the triangle, Figure 3). This diffusional growth mechanism has been treated extensively and, therefore, is not dealt with here.

Finally, by aggregation of nanosize subunits one can obtain polycrystalline particles of *spherical or other shapes* (the right hand side at the bottom of the triangle, Figure 3).

AGGREGATION MECHANISM

The aggregation mechanism is by now established to be quite general, leading to a large variety of particles in terms of composition, structure, size, and shape. Consequently, it deserves special attention, but it also involves many challenges, especially if the formation of uniform particles is to be explained, and even more so when their appearance in different shapes is being considered. One essential aspect of this mechanism is that the resulting polycrystalline particles can be of any shape, including spheres.

In principle, once the nanosize stage is reached, the conditions must allow the particles to aggregate, which

means that the dispersion needs to be destabilized. If the stability of dispersions crystallites is due to electrostatic repulsion, the latter must be eliminated, which may happen, for example, if during the precipitation process the pH of the system is shifted towards the isoelectric point, or if the ionic strength becomes high enough to sufficiently compress the double layer. However, these changes by themselves do not account for particle uniformity. The challenge is to establish conditions which must be fulfilled to achieve size selection. This task was carried out in order to model the formation of uniform spheres by aggregation, and it was tested on colloidal metals and compounds,^{17,18} as exemplified with silver in the next section.

Formation of Monodispersed Spheres by Aggregation

The spherical silver particles shown in Figure 4 were prepared by adding rapidly 100 cm³ of a 0.02 mol dm⁻³ ascorbic acid solution under vigorous mixing into 300 cm³ solution containing 0.04 mol of AgNO₃ and 0.08 mol of ethylene diamine. The resulting spheres, approximately 0.9 μm in diameter, were formed in less than 15 seconds. The color changes observed in the early stages of the process were a clear indication that highly dispersed

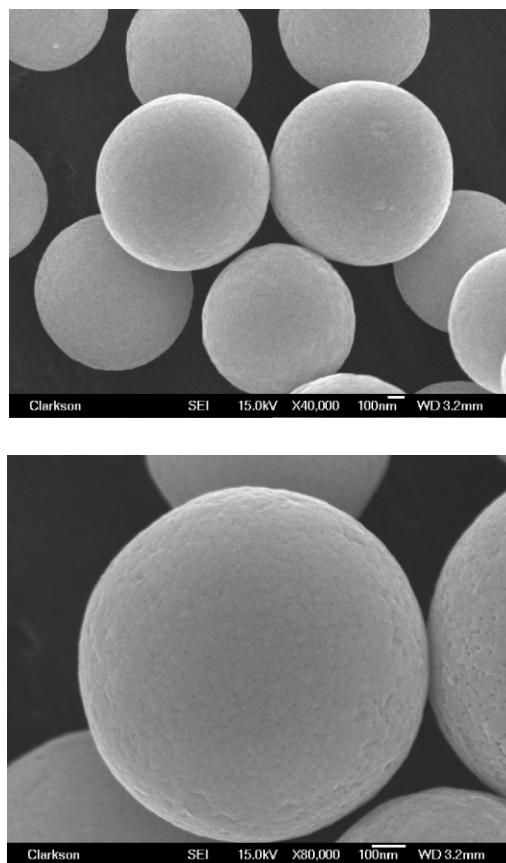


Figure 4. Field emission electron micrographs at two magnifications of spherical polycrystalline silver particles obtained by reducing a silver diamine complex with ascorbic acid.

silver nanoparticles (the precursor subunits) were generated first in the system and later aggregated to larger polycrystalline silver spheres. The size of the subunits in the final solids estimated from the XRD data (Figure 5) was found to be ≈ 16 nm.

The formation of the polycrystalline Ag particles of spherical shape as a result of the aggregation mechanism is rather easy to rationalize. Once the energy barrier between the nanosize precursors is eliminated as a result of one of the causes mentioned in the preceding section, a burst of a finite number of »aggregation centers« occurs, which grow rapidly at the expense of the surrounding constituent subunits. Since the process is rather rapid and the subunits do not have sufficient time to rearrange, the shape of the resulting aggregates is spherical and their size is determined by the number of the aggregation centers and the concentration of the precursor nanoparticles.

A more difficult task, however, is to explain when will the aggregation process yield *uniform* spheres. A model which accounts for this rather unexpected outcome was developed by Privman, Goia, and Matijević based on the investigations of the formation of polycrystalline spheres of gold.¹⁷ The study has revealed that the growth of the final particles by the aggregation of singlets must be coupled with the rate of formation of the precursors. Numerical calculations have indicated that, if the concentration of the latter were constant, *i.e.* if they were continuously generated to compensate for their depletion due to aggregation, the size distribution would be broad and would peak at small diameters. However, if the concentration of primary particles decreases with time, size selection can occur. The model developed assumes that the diffusion constant of singlets is considerably larger than of the aggregates so that the attachment prevails. The standard rate equation then reads

$$\frac{dN_s}{dt} = w_{s-1}N_{s-1} - w_s N_s, \quad \text{for } s > 1 \quad (1)$$

where $N_s(t)$ is the time dependent density of secondary particles containing s primary particles.

In normal approaches to aggregation the evolution of the population of singlets, which is not covered by Eq. (1), is obtained by the conservation of matter

$$N_1(t) + \sum_{j=2}^{\infty} jN_j(t) = N_1(0) \quad (2)$$

which assumes that at $t = 0$ there are only singlets. Equations (1) and (2) need to be modified to conform by introducing a term that accounts for the rate $\rho(t)$ at which primary particles are formed per unit volume. Consequently, the $N(t)$ is expressed by replacing Eq. (2) with

$$N_1(t) = \int_0^t \rho(t') dt' - \sum_{j=2}^{\infty} jN_j(t) \quad (3)$$

with initial values of $N_s(0) = 0$ for all $s = 1, 2, 3, \dots$ from classical nucleation theory.

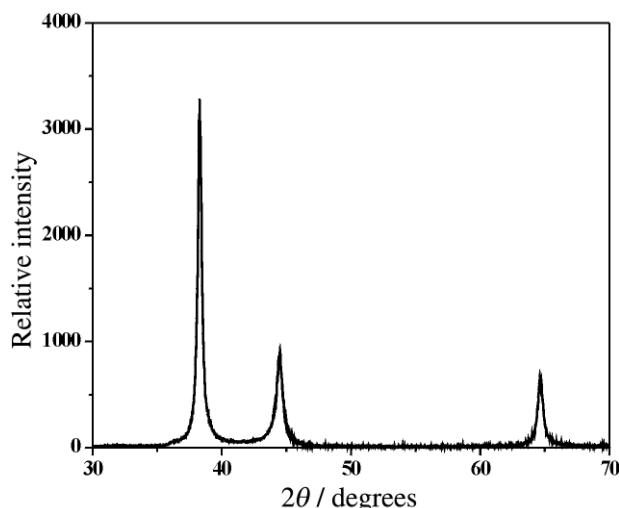


Figure 5. The X-Ray pattern of silver polycrystalline particles shown in Figure 4.

The expression for $\rho(t)$ was then developed, which includes experimentally accessible parameters, as described in detail¹⁷

$$\rho(t) = \frac{32\pi^2 a^3 \sigma D c^2}{3kT \ln(c/c_0)} \exp \left\{ -\frac{256\pi^3 a^6 \sigma^3}{27(kT)^3 [\ln(c/c_0)]^2} \right\} \quad (4)$$

where $c(t)$ is the concentration of solute, species (atoms, ions), which serve as monomers for primary particles nucleation, while c_0 is its equilibrium saturation concentration. Finally, σ is the effective surface tension of the singlets.

When all known parameters for silver (except for the value of σ , which is not known with certainty) were inserted in the model, the calculations yielded an average particle size of 0.9 μm for the silver particles shown in Figure 4, in very good agreement with the electron microscopy data.

Particles of Nonspherical Shape by Aggregation

There are numerous challenges to be overcome in order to resolve the formation by aggregation of uniform particles of shapes different than spherical. To do so, one should first consider chemically simple compounds precipitated in solutions of as few solute complexes as possible, although even in such cases some unexpected observations were reported. For example, one would expect that the final particle morphology may be determined by the shape of the precursor constituents. While this was indicated in some cases, such as in the formation of hematite (Fe_2O_3),¹⁹ no general rules have been established. For example, monodispersed gold spheres¹⁹ are formed by aggregation of anisometric subunits, while some elliptical copper oxide particles are made up of spherical building blocks.²⁰ Also, the charge characteristics, such as their distribution along the faces and edges of these

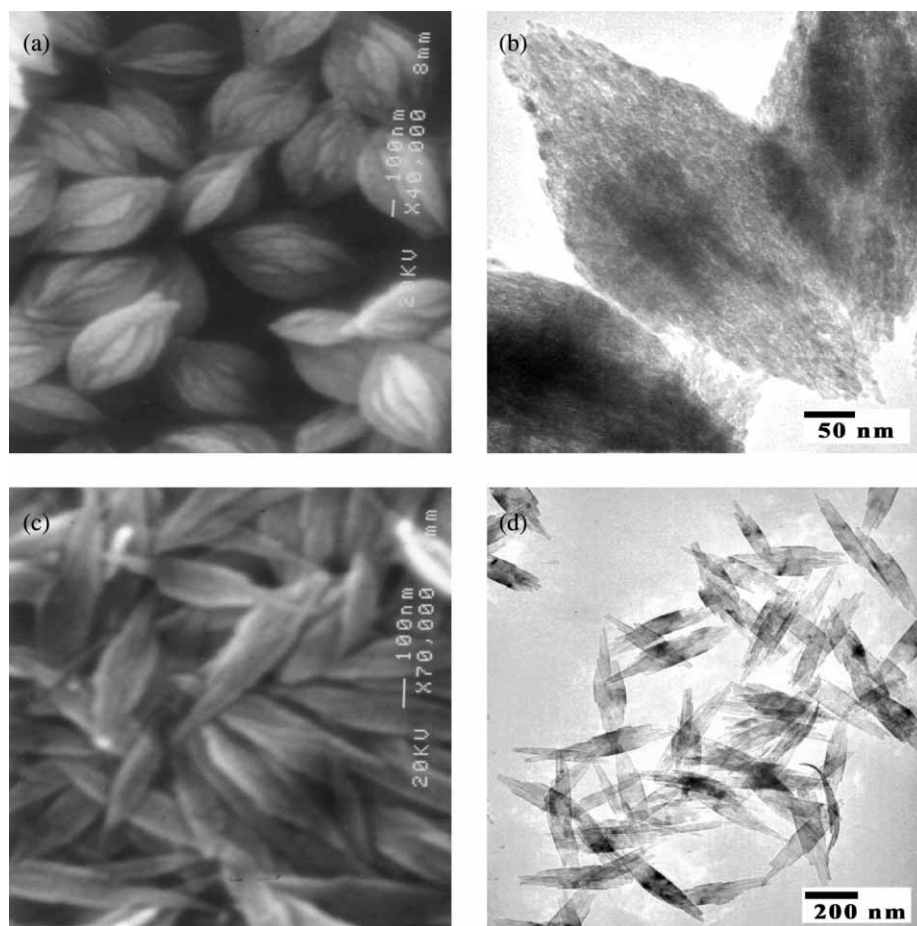


Figure 6. (a) and (c): Scanning electron micrographs of CuO particles obtained by the controlled double jet precipitation in solutions of $\text{Cu}(\text{NO}_3)_2$ and NaOH in molar ratio 1:1 and 3:1, respectively. (b) and (d): Transmission electron micrographs of the corresponding systems in (a) and (c).

primary particles, must play a role in the aggregation process, but neither of these effects alone is sufficient to explain the observed systems.

To gain some insight into the various parameters that may affect the particle morphology two systems are presently being investigated, *i.e.* copper (hydrous) oxide and magnesium (sodium) fluoride. These compounds are of relatively simple chemical compositions and readily obtained in specific shapes.

Copper Oxide. – Colloidal copper oxide particles of different shapes have been described earlier,^{20–22} which indicated their formation by aggregation of nanosize subunits. Additional study on the precipitation of CuO by controlled double jet precipitation process (CDJP) is described here. As before, such well defined dispersions can be obtained by simply mixing solutions of Cu^{II} nitrate and sodium hydroxide. Specifically, a 0.01 mol dm^{-3} $\text{Cu}(\text{NO}_3)_2$ solution and NaOH solutions in concentrations ranging from 0.1 to 0.02 mol dm^{-3} were simultaneously introduced by peristaltic pumps into the CDJP reactor containing 50 cm^3 of deionized water at a constant flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$ for 50 s, followed by aging either at $50 \text{ }^\circ\text{C}$ or at room temperature for extended periods of time. To

study the particle growth dynamics, suspension samples were withdrawn from the reactor at different times during the aging, and the solids separated by filtration.

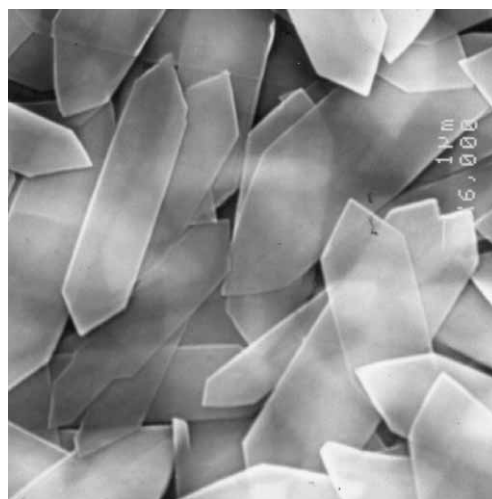


Figure 7. Electron micrograph of CuO particles shown in Figure 5 after aging the aqueous dispersions at room temperature for extended period of time.

The particle shapes could be altered by the ratio of reactant concentrations, the anion of the copper salt (nitrate, halide, or sulfate), and temperature of the post-treatment of the rapidly precipitated but fully dispersed solids in the mother liquor.

The particles obtained at two different molar ratios of $\text{Cu}(\text{NO}_3)_2/\text{NaOH}$ given in the legend, are illustrated in Figures 6a and 6c. While the morphology of the dispersed solids differs, it is clearly demonstrated that they are composed of nanosize subunits (Figures 6b and 6d). The size of these precursors, estimated from electron micrographs, is ≈ 10 nm, while from X-ray diffraction patterns it was calculated to be 13 nm. The composition of these samples was shown to be CuO .

Prolonged aging dispersions prepared as given in Figure 6 at room temperature (22°C) yielded hexagonal particles of high crystallinity (Figure 7) which showed no substructure, similar to what was obtained before by aging solutes of $\text{Cu}(\text{NO}_3)_2$ in the presence of urea.²² Obviously, the slow aging process in the present case resulted in structural transformation of the particles as was indicated as a path by the bottom line of the scheme in Figure 1.

MgNaF₃ (Nighborite). – It was shown in an earlier study that mixing solutions of MgCl_2 and NaF produced on

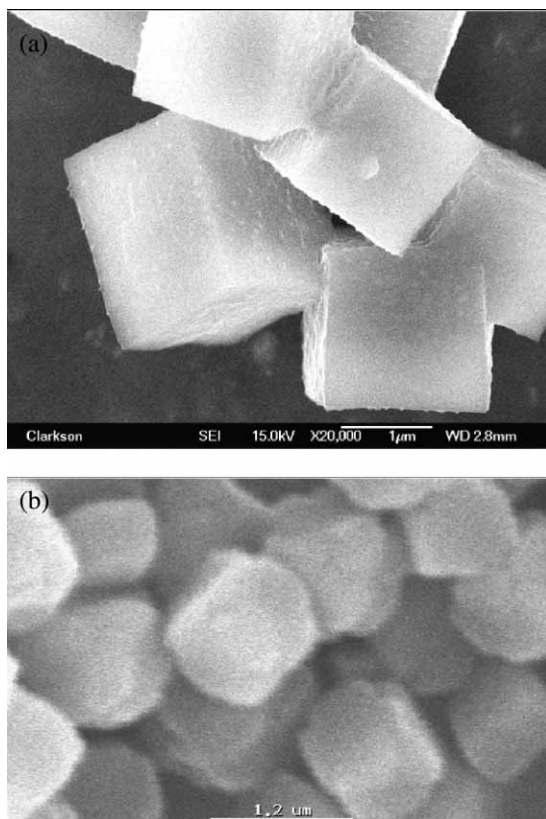


Figure 8. MgNaF_3 particles prepared by mixing solutions of 0.01 mol dm^{-3} MgCl_2 and 0.1 mol dm^{-3} NaF aged at (a) 80°C and (b) 40°C .

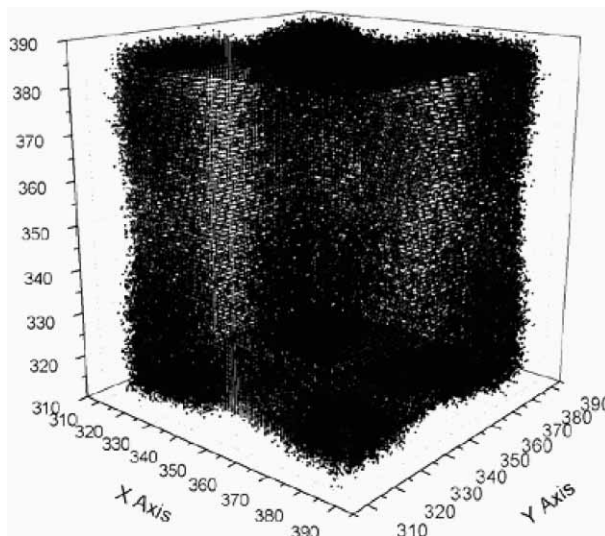


Figure 9. Computer model for the formation of MgNaF_3 particles shown in Figure 8b.

aging uniform polycrystalline cubs, which appeared as ideal to study the mechanism of the formation of particles of such simple shape.²³ Additional comprehensive experimental investigations have proven this precipitation process to be more involved than anticipated.

In a typical experiment 0.2 mol dm^{-3} solutions of MgCl_2 and NaF , preheated to 80°C were mixed in a 10:1 NaF/MgCl_2 volume ratio. Rapidly, a white precipitate is formed which consisted of spheres, clearly built of small subunits, identified by X-rays diffractograms to be MgF_2 . On continued aging of the same system at elevated temperatures, these solids underwent phase transformation into cubic MgNaF_3 particles (Figure 8). Exposing these particles by electron beam disclosed their substructure of primary nanosize constituents.

At this stage initial numerical modeling has been initiated to explain the formation of cubic particles from small precursors. The process is based on two stages:

- (a) Deposition of the building blocks on the surface of the »primary particle« located in a three-dimensional space, and
- (b) Rearrangement of the particles arriving at the surface at the spot closest to the center of the surface.

Based on these premises, Figure 9 shows the shape evolution of the critical particle in three dimensions, which has a close resemblance with the cubes of MgNaF_3 at the earlier stages of aggregation at 40°C (Figure 8b).

Acknowledgements. – This study was supported by the NSF grant DMR-0509104. The authors are acknowledging graduate students Brendan Farrell, Igor Sevonkaev, Sergei Libert, and Ionel Halaciuga for their experimental work described in this article. The article is dedicated to Professor Nikola Kallay, a friend and collaborator.

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SAŽETAK

Mehanizam nastajanja jednolikih koloidnih čestica

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Prikazani su različiti mehanizmi nastajanja jednolikih koloidnih čestica precipitacijom iz homogenih otopina. Ti su mehanizmi odgovorni za strukturu i oblik nastalih čestica. Posebno su razlikovani uvjeti nastajanja (a) amorfnih sfera, (b) nesferičnih kristalnih čestica različitih oblika i (c) polikristalnih čestica različitih morfologija (uključujući sfere). Ustanovljeno je da polikristalne čestice nastaju agregiranjem nanometarskih prekursora daleko češće nego što se to prije mislilo. Model koji objašnjava nastajanje jednolikih sfera određenih veličina ilustriran je na primjeru čestica srebra. Nastajanje jednolikih polikristalnih čestica različitih oblika objašnjeno je također agregacijskim procesom. Prikazan je pokušaj semi-kvantitativnog predskazivanja oblika koloidnih čestica.