Preparation and Properties of Uniform Size Colloids

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Received December 16, 1992. Revised Manuscript Received February 11, 1993

The achievements and problems in the preparation of uniform colloids by precipitation from homogeneous electrolyte solutions are reviewed. Specifically, the syntheses of "monodispersed" particles of simple and mixed composition as well as of coated and hollow particles of different shapes are described, and the physical and chemical mechanisms of their formation are discussed.

Introduction

The title of this review article, as suggested by the editor, requires clarification. The science of colloids deals with matter of large specific surface areas, regardless of the state (solid, liquid, gas) or morphology (films, fibers, particles). Here, the emphasis is on finely dispersed solids, which needs further specification. The "size boundaries" implicit in colloids are a subject of contention. While everyone agrees that a particle in the micrometer range is typical of this state of matter, the definition becomes vague when considering very small (e.g., 10 Å) or much larger (many micrometers) dispersed solids. Presently a rather active and exciting area of research deals with the so called "quantum-size" (nanosize) particles[1] and the philosophical question arises, when a system ceases to be colloidal, i.e., when it should be considered a molecular cluster or an "ionic complex".

This review is restricted to particles typically of a few hundred nanometers to a few micrometers. The matter so dispersed is very common in nature; it appears as volcanic ash, haze, interstellar dust, mud, clay, and other minerals (especially distributed in natural waters), etc. Such colloids are also byproducts of many industrial operations. More importantly, they are essential in numerous technological and medical applications, such as in ceramics, pigments, recording materials, electronics, catalysis, medical diagnostics, drug delivery systems, and countless others. As the specifications in these uses become more stringent, the need for better defined solids, in terms of the particle composition, size, and shape, increases. The magnetic, optical, electric, adsorptive, catalytic, and other properties often depend strongly on the morphology and various physical characteristics of the dispersed matter, in addition to its chemical composition. Therefore, it is of no surprise that the interest in fine particle science has increased considerably in recent years.

Several techniques have been developed, some based on physical, others on chemical, and yet some on both kinds of principles, capable of producing "monodispersed" colloids. It would be impractical to describe in an article of limited scope all the different procedures presently in use for this purpose. Instead, this review is concerned with conditions that yield uniform particles by precipitation from homogeneous solutions and with modifications of their properties by subsequent treatments, which can be designated as phase transformations.

Considerable success has been achieved in terms of the variety of well-defined colloids obtained in aqueous electrolyte environments. Such dispersions can consist of particles of simple or mixed composition, of many shapes, and over a range of modal sizes. It is also possible to generate coated particles with shells chemically different from the cores. Finally, the preparation of hollow inorganic spheres has recently been described. Some of these results have been summarized in a series of articles published in two special issues of the *MRS Bulletin*[2] and in several review articles.[3-9]

The availability of "monodispersed" colloids not only has made it possible to evaluate many properties of matter in finely dispersed state but also has opened up some challenging questions, which need yet to be satisfactorily answered. Of particular significance are problems related to the dependence of the particle morphology and structure on the experimental conditions, especially with respect to chemical speciation of complexes leading to the precipitation in a given solution. Another set of fundamental queries to be resolved refers to the mechanisms of the processes that follow the nucleation stage. Some of these aspects of the formation of uniform particles will be addressed in this review.

The number of publications on monodispersed colloids has increased dramatically in recent years. Thus, a comprehensive coverage of all studies would be impractical in a single article. Instead, essentially a self-review is offered here.

Historic Note

It may be of interest to recognize that only very few examples of well-defined colloids have been found in nature. Probably, the best known are opals, which are composed of monodispersed spherical silica particles.[10] Another, less common natural system, consisting of uniform octahedral iron sulfide embedded in shale, is illustrated in Figure 1.[11]

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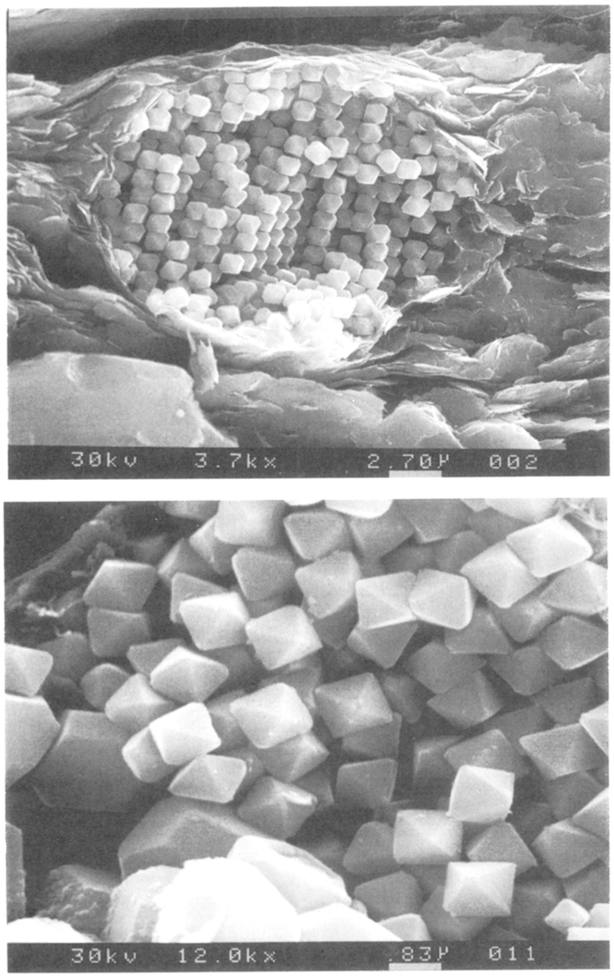

Figure 1. Scanning electron micrographs (SEM) of colloidal iron sulfide embedded in black shale.[11] Courtesy Professor Neal R. O'Brien, New York State University at Postdam.

The descriptions of preparations and of some properties of synthetic "monodispersed" colloids are not new in the literature. Indeed, they date back to Faraday, who produced gold sols of different colors and recognized their particulate character,[12] extensively studied since.[13,14] Several different dispersions of other colloidal elements had been prepared, such as LaMer's sulfur sols,[15,16] used in detailed evaluation of their optical properties.[17] Uniform spherical particles of selenium were obtained and analyzed by Watillon and associates.[18,19]

Some compounds were also generated as particles uniform in size and of different shapes. For example, ellipsoidal barium sulfate[20,21] and spherical metal iodates[22] were precipitated from aqueous metal salt solutions in the presence of different additives. However, the majority of studies have dealt with monodispersed silver halides, which is not surprising in view of the significance of these materials in photography. Exceedingly uniform particles in a variety of shapes have been obtained by several investigators,[23,24] exemplified by a silver bromide powder in Figure 2.[24]

Least success was recorded with the most important inorganic compounds, i.e., metal and nonmetal (hydrous) oxides. Only a few such uniform colloidal dispersions had been successfully prepared in the past, prominent among which were elongated crystals of β-FeOOH produced by Heller and associates,[25,26] who investigated their schiller layers.[27,28] Tungstic oxide is another monodispersed system, obtained by Furusawa and Hachisu,[29] used in the evaluation of its optical properties[30] and of long-range forces between colloid particles.[31] Spherical silica particles have been synthesized, which are as uniform in size as the best polymer latexes.[32,33]

While this short discussion of older studies is by no means exhaustive, the described preparations have one thing in common: they offer no underlying physical or chemical principles (except for silica) that would allow either for the generalization of the processes involved or for the development of an understanding of the mechanisms of the formation of monodispersed particles. One needs to inspect the only laboratory text[34] written strictly for colloids (long out of print) to recognize that all procedures for the precipitation of finely dispersed matter read like "cookbook" chemistry.

The purpose of this review is to describe more recent advances in the field of well-defined colloids, generated by the precipitation from homogeneous solutions, and to point out some of the problems that need yet to be addressed.

Metal (Hydrous) Oxides and Non-Oxides

This section is arbitrarily divided into description of uniform metal (hydrous) oxide and metal non-oxide compounds.

Metal (Hydrous) Oxides. The above-mentioned paucity of information on the preparation of monodispersed metal (hydrous) oxides is readily understood, if one recognizes the sensitivity of the properties of generated solids on the experimental conditions. The chemical composition and the morphology of the resulting particles depend on a number of parameters, which often need to be changed only slightly in order to alter the nature of such precipitates. Some of these conditions are quite obvious, while others are not. As a rule, it is necessary to carefully control the pH, concentration of the reactants, temperature, anions of a given metal salt solution, method of mixing, etc., in order to duplicate a synthesis. This sensitivity also puts special demands on engineers who may wish to scale up the precipitation procedures or

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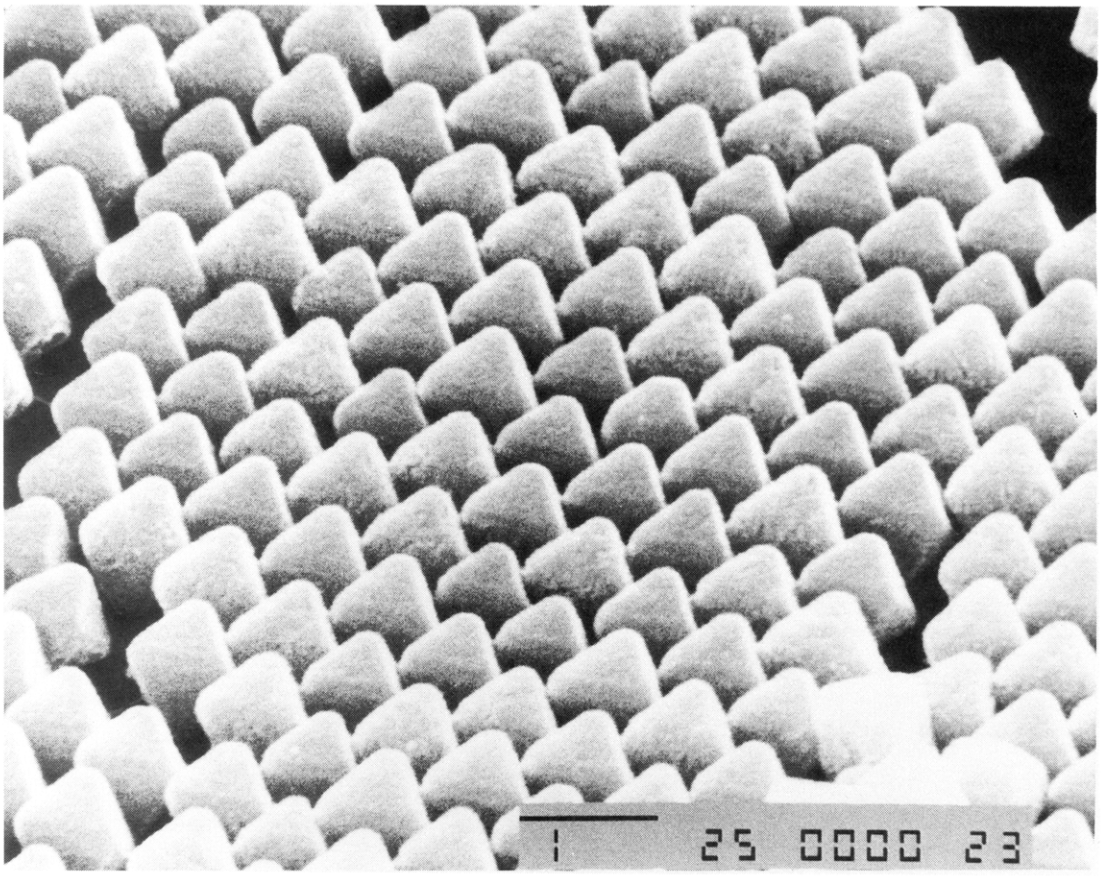

Figure 2. SEM of monodispersed silver bromide particles.[24] Courtesy Dr. Joe E. Maskasky, Eastman Kodak Co., Rochester, NY.

develop continuous processes for the preparation of metal (hydrous) oxides. For example, in most cases it is not possible to substantially increase the reactant concentrations to produce larger amounts of the material or to raise temperature to speed up a process, because different products may result.

To illustrate the above points, Figure 3 displays the precipitation domains obtained when the pH is altered by the addition of a strong base to aqueous $CuSO_4$ solutions at two different temperatures, the details of which are described in the legend.[35] It is noteworthy that a small change in the salt concentration or in the pH over critical regions produces particles of different chemical composition and morphology. These boundaries are also dependent on temperature. The role of anions is evident, if one compares Figures 3 and 4, which differ only in the copper(II) salt used under otherwise identical conditions. In the presence of $Cu(NO_3)_2$ the generated solids, their particle shape, and the precipitation regions are unlike those obtained with $CuSO_4$. In no case were uniform dispersions achieved by the employed procedure.[35]

It is difficult, if not impossible, to generate "monodispersed" metal (hydrous) oxides by the addition of a strong base into the solution of a metal salt. To control the kinetics of metal ion hydrolysis, that will eventually result in uniform particles, one may proceed in three different ways: (A) forced hydrolysis; (B) controlled release of hydroxide ions; (C) decomposition of organometallic compounds.

(A) Forced Hydrolysis. In this procedure aqueous salt solutions are aged at elevated temperatures, usually over the range 80–100 °C, for different periods of time, which depend on the hydrolyzability of the cation in question. As a result, the pH decreases in course of the reaction due to the deprotonation of the hydrated cations, eventually leading to the formation of solid hydrous oxides. Uniform particles of a given chemical composition, morphology, and structure are normally precipitated under a restricted range of conditions and are strongly dependent on the presence of certain anions. The latter may either be incorporated in a stoichiometric amount, giving a stable basic metal salt, or be present as contaminants in varying amounts, which can be leached out by rinsing with water or mild acids or bases.

Several electron micrographs are offered to illustrate some of the dispersions obtained by forced hydrolysis. Figure 5a,b shows particles of aluminum[36] and chromium hydroxide,[37] respectively, prepared under conditions given in the legend. In both cases sulfate ion was needed to obtain uniform spheres, which were amorphous. Dispersions illustrated in Figure 5c,d are of cerium(IV) oxide[38] and iron(III) oxide,[5,39,40] respectively. The last two kinds of spherical particles differ from the former two examples in terms of their structure. The X-ray diffraction (XRD) pattern of CeO_2 shows a face-centered cubic crystal lattice, while that of iron oxide is characteristic of hematite (α-Fe_2O_3). A careful examination of these apparently crystalline spheres shows that they consists of aggregates of much smaller subunits. The finding that uniform larger particles have a substructure is quite general and will be discussed in more detail later.

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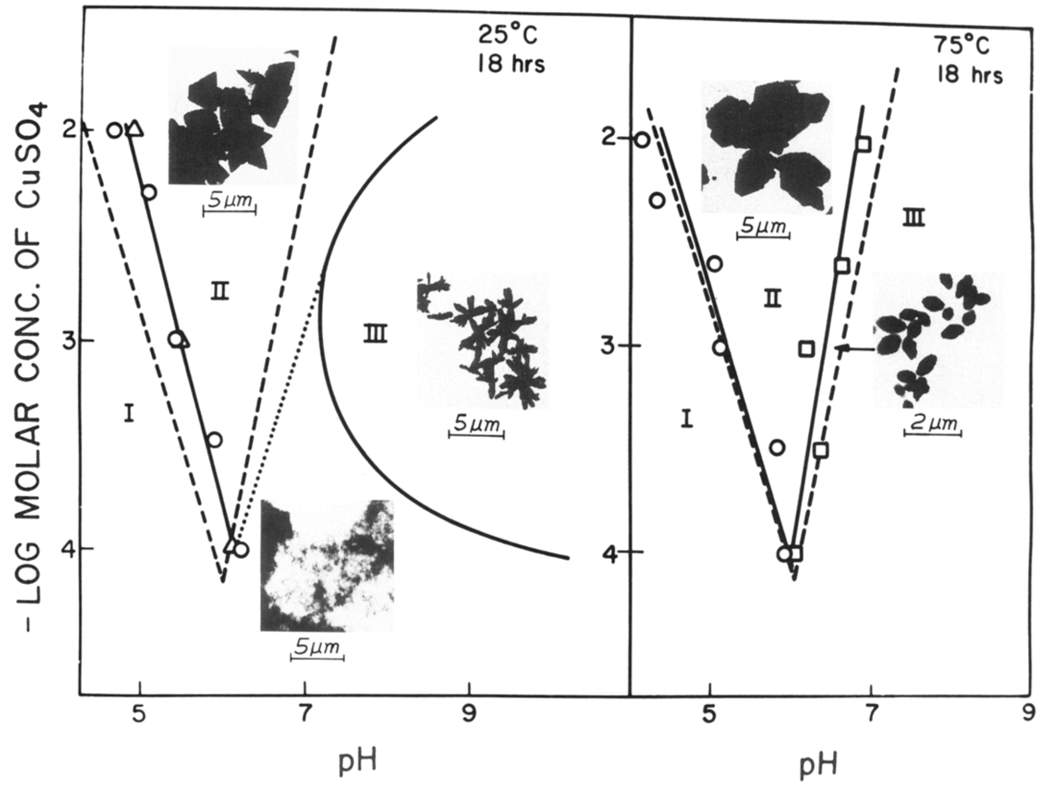

Figure 3. Precipitation domains determined with aqueous copper(II) sulfate solutions as a function of the pH for systems aged for 18 h at 25 °C (left) and 75 °C (right), respectively. Regions: I, homogeneous solution; II, blue precipitate (brochantite); III, red-brown precipitate (tenorite). Solid lines indicate boundaries between various regions, the individual experimental points being represented by circles and squares. Triangles indicate data obtained with the ion-specific electrode. The expected phase transitions are shown by dashed lines; the dotted line indicates the boundary between areas of large and small particles within region II at 25 °C. Electron micrographs show particles typical of those formed throughout the corresponding region except for the one at the extreme right, for which the preparation conditions are indicated by the arrow.[35]

Forced hydrolysis can also yield particles of other shapes, either of the same or different chemical composition. Figure 6b,c illustrates cubic[41] and ellipsoidal[42] particles of hematite, both precipitated in $FeCl_3$ solutions. In the latter case, the acyclic morphology was achieved by the addition of a small amount of phosphate ions, which are not incorporated in the solids. A precipitate of different chemical composition can be obtained from ferric chloride solutions, if the conditions are altered, as illustrated in Figure 6a on the example of rodlike akageneite (β-FeOOH),[39] or of particles of mixed α-Fe_2O_3 and β-FeOOH composition (Figure 6d).[43] The so-prepared solids contain different amounts of Cl^- as contaminants, which can be removed by extensive washings.[44]

The described dispersions can be readily reproduced but not a priori predicted. Instead, precipitation domains as shown in Figure 7 are offered to indicate conditions for the preparation of particles of given compositions and morphologies.[39]

It is also noteworthy that the so obtained iron(III) (hydrous) oxides can be reduced either to pure metals[45,46] or partially reduced to magnetite and reoxidized to maghemite,[47] without changing their particle shapes.

On aging acidifed ferric sulfate solutions, the anion is permanently incorporated in the solids, yielding a stoichiometrically well-defined colloidal basic ferric sulfate, $[Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O]$ (Figure 8), which has the composition of jarosite, established by chemical analysis and confirmed by XRD.[48]

With less strongly hydrolyzable cations, it is necessary to somewhat raise the pH by the addition of a weak base in order to promote the precipitation. The nature of the base, however, may also affect the properties of the resulting particles, as illustrated in Figure 9, which displays different ZnO dispersions, all of which showed XRD patterns characteristic of zincite.[49]

The offered examples are just a few selected from a large number of "monodispersed" metal hydrous oxides prepared by forced hydrolysis.

(B) Controlled Release of Hydroxide Ions. Rather than to deprotonate hydrated metal ions, which is the major reaction in the above-described procedure, the hydrolysis of cations can be controlled by a slow release of hydroxide ions into a metal salt solution. The decomposition of certain organic compounds, such as urea or formamide, has been extensively used for this purpose. In the case of urea, carbonate ion is produced accompanied by a simultaneous increase in the pH, which often leads

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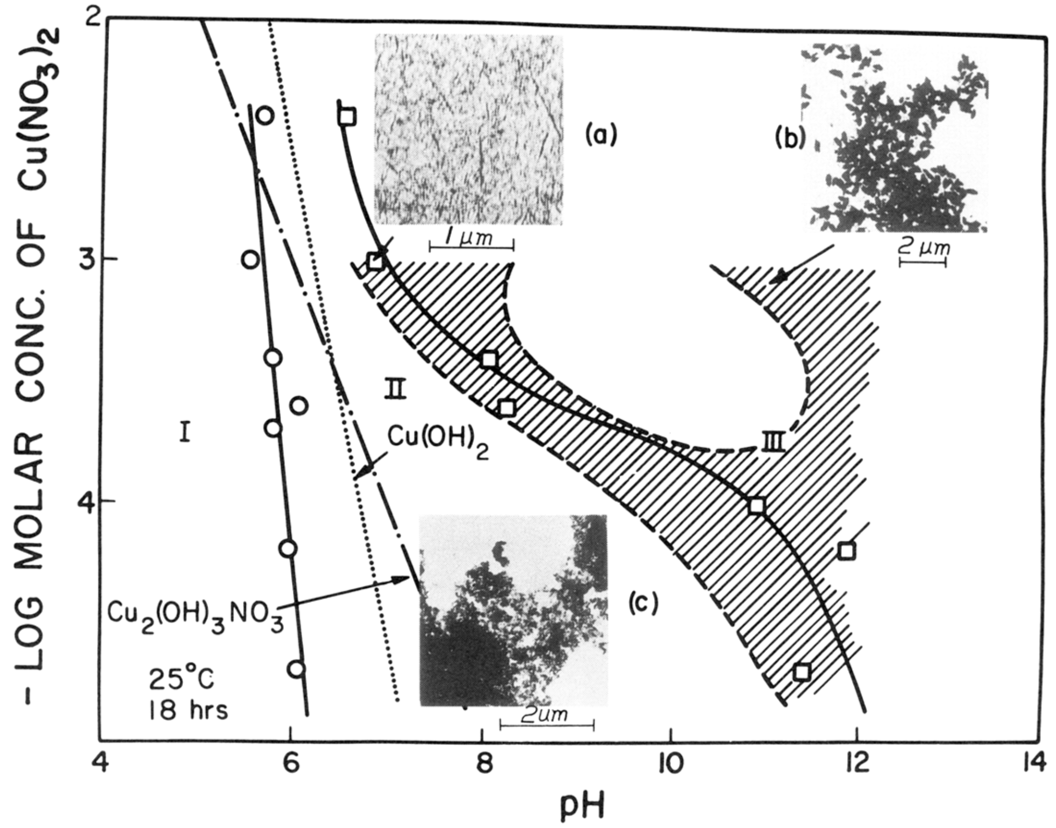

Figure 4. Precipitation domain determined with aqueous solution of copper(II) nitrate as a function of the pH for systems aged for 18 h at 25 C. Regions: I, homogeneous solution; II, blue precipitate; III, red-brown precipitate. The shaded area indicates the formation of stable sols. Electron micrographs show typical particles from various regions. The dashed–dotted and the dotted lines are calculated solubility boundaries for the copper basic nitrate and hydroxide, respectively.[35]

to the precipitation of metal basic carbonates. The latter can be transformed to metal oxides by calcination, and if the heating is carefully carried out, the morphology of the particles is preserved.

A list of colloids so prepared in the presence of urea is given in ref 50. In particular, the method lends itself well for the synthesis of different lanthanide compounds.[51,52] Figure 10 illustrates two dispersions obtained by aging YCl_3 solutions in the presence of urea, which also demonstrates that just changing reactant concentrations and temperature can yield particles that differ in both composition and morphology.[53] The amorphous particles of $Y(OH)CO_3$ (Figure 10a) are readily converted to spherical Y_2O_3 by calcination at elevated temperatures.

The properties of dispersions can also be greatly affected by the nature of anions as documented on the example of copper(II) compounds (Figure 11).[54,55] Similarly, cobalt, zinc, ruthenium, palladium, and zirconium compounds of different compositions and morphologies were obtained by aging the corresponding metal salt solutions in the presence of urea or formamide.[56–59]

(C) Decomposition of Organometallic Compounds. The most common starting organometallic compounds used in the preparation of metal (hydrous) oxides are various alkoxides, which readily hydrolyze at low temperatures by the addition of water. The properties of the resulting particles can be controlled by the concentration of alcoholic alkoxide solutions, the amount of water, and the rate by which the latter is admixed. Under proper conditions uniform amorphous spherical particles of different modal diameters are obtained and, therefore, there is no need to illustrate them here. This technique has been used to prepare a number of colloidal metal (hydrous) oxides, including those of aluminum,[60] titanium,[61,62] zinc,[63] and zirconium.[63] It should be noted that the natures of the products also depend on the alkoxide ligand bound to a given metal.

Probably the most extensively investigated such process deals with the synthesis of silica by the hydrolysis of tetraethoxy silane (TEOS) first described by Stöber et al.[32] and later on modified and examined by a number of investigators.[33,64–66]

In an entirely different approach metal chelates or similar organometallic compounds can be decomposed in alkaline solutions to yield uniform metal oxides. Most products so prepared appear as particles of different crystal

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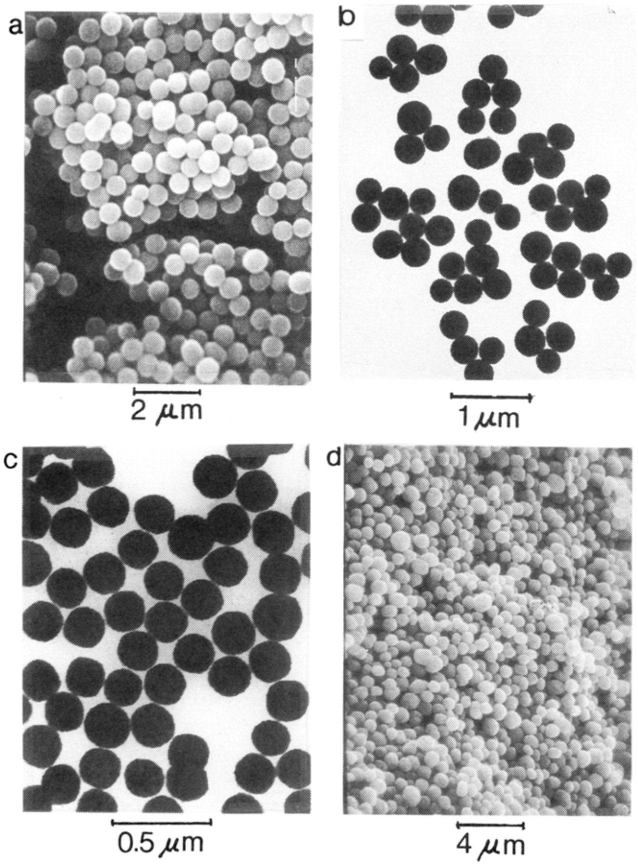

Figure 5. Electron micrographs of (a) aluminum (hydrous) oxide obtained by aging at 105 °C for 24 h a solution of 2.0×10^{-3} mol dm^{-3} $Al(NO_3)_3$ and 3.0×10^{-3} mol dm^{-3} $(NH_4)_2SO_4$;[36] (b) chromium (hydrous) oxide particles obtained by aging at 75 °C for 24 h a solution of 4.0×10^{-3} mol dm^{-3} $CrK(SO_4)_2{\cdot}12H_2O$;[37] (c) cerium(IV) oxide particles obtained by aging at 90 °C for 48 h a solution of 1.2×10^{-3} mol dm^{-3} $Ce(SO_4)_2$ and 8.0×10^{-2} mol dm^{-3} H_2SO_4;[38] and (d) hematite (α-Fe_2O_3) particles obtained by aging at 100 °C for 10 days a solution of 3.2×10^{-2} mol dm^{-3} $FeCl_3$ and 5.0×10^{-3} mol dm^{-3} HCl.[5,39]

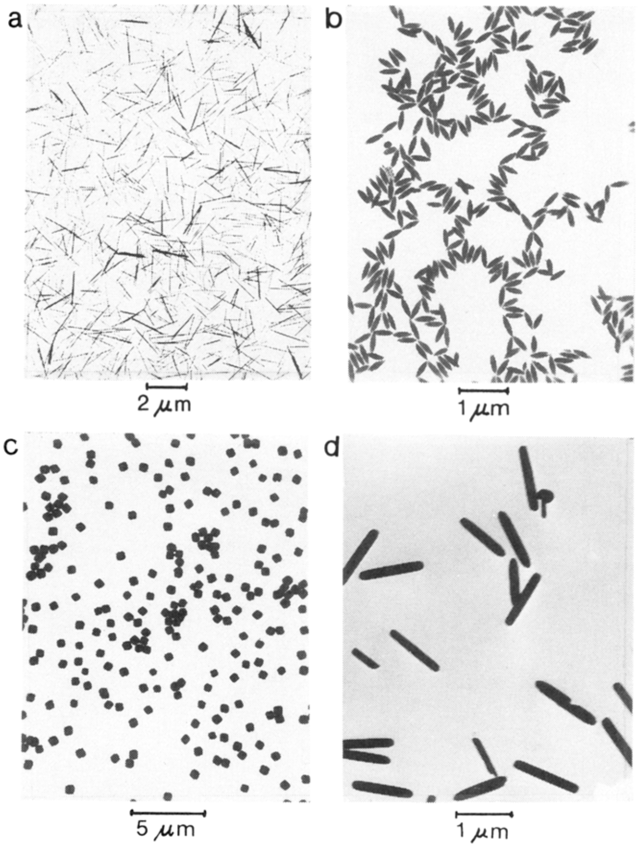

Figure 6. Transmission electron micrographs (TEM) of (a) akageneite (β-FeOOH) particles obtained by aging at 100 °C for 24 h a solution of 4.5×10^{-3} mol dm^{-3} $FeCl_3$ and 0.10 mol dm^{-3} HCl;[39] (b) hematite (α-Fe_2O_3) particles obtained by aging at 100 °C for 48 h a solution of 2.0×10^{-2} mol dm^{-3} $FeCl_3$ and 3.0×10^{-4} mol dm^{-3} NaH_2PO_4;[42] (c) hematite particles obtained by aging at 100 °C for 16 h a solution of 1.9×10^{-2} mol dm^{-3} $FeCl_3$, 1.2×10^{-3} mol dm^{-3} HCl, and 40% (vol) ethanol;[41] and (d) rodlike particles of a mixed α-Fe_2O_3 and β-FeOOH composition obtained by aging at 100 °C for 48 h a solution of 1.8×10^{-2} mol dm^{-3} $FeCl_3$, 3.0×10^{-2} mol dm^{-3} HCl, and 20% (vol) ethylene glycol.[43]

shapes, rather than spheres, and usually are much larger in size than obtained by other procedures. For example, well-defined copper(II) oxide dispersions of different morphologies were generated by heating complex copper tartrate (Fehling) solutions in the presence of glucose,[67] as illustrated in Figure 12.

The decomposition of metal chelates require, as a rule, much higher temperatures because of the stability of these complexes. Figure 13 exemplifies two such dispersions; the first consists of disklike hematite (α-Fe_2O_3) particles,[68] while the other shows crystals of Co_3O_4 precipitated by heating the corresponding metal complex solutions at 250 °C in steel tubes lined with Teflon.[69]

Metal Non-oxides. Analogous procedures as described in previous sections can be applied to the formation of uniform inorganic colloids different than oxides. Several metal sulfides were obtained either by bubbling H_2S through metal chelate solutions or by decomposition of thioacetamide in aqueous electrolytes.[70–74] In the latter case the successful synthesis of monodispersed particles was conditioned by the controlled release of sulfide ions. Electron micrographs in Figure 14 display zinc sulfide[72] and lead sulfide[73] dispersions so generated. The perfectly spherical ZnS particles exhibited an X-ray diffraction pattern characteristic of crystalline sphalerite. Less surprising is that the lead sulfide was identified as galena.

In a similar manner colloidal cadmium and lead selenides were synthesized by decomposition of selenourea in corresponding metal salt solutions.[75]

Dispersions consisting of spherical amorphous particles of (basic) phosphates of aluminum,[76] iron,[77] zinc,[78] cobalt,[79] cadmium, nickel, and manganese(II)[80] were obtained by aging electrolyte solutions containing phosphate ions. The TEM of the last dispersion is illustrated in Figure 14c.

The final example (Figure 14d) shows cadmium carbonate, $CdCO_3$, crystals prepared by interaction of a $CdCl_2$ solution with urea.[81] On calcination this solid yields

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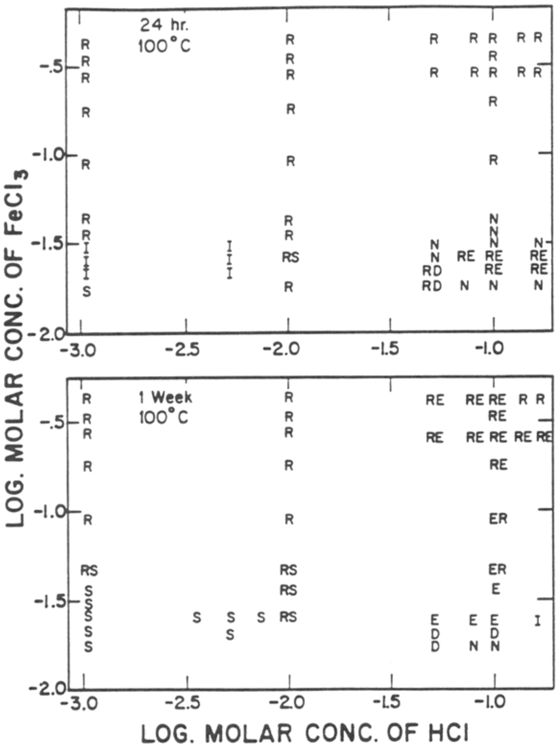

Figure 7. Concentration domains of solutions containing $FeCl_3$ and HCl aged at 100 °C for 24 h (upper) and for 1 week (lower). Symbols: N, no particle formation. Particle shapes: D, double ellipsoidal; E, ellipsoidal; I, irregular of varying sizes; R, rodlike; S, spherical. Pairing of symbols indicates a mixture of corresponding particles in the suspension. Particle composition: R, β-FeOOH; all other particles, α-Fe_2O_3.[39]

CdO without altering its morphology. As a result the specific surface area changes from 1.8 $m^2 g^{-1}$ for the original to 22 $m^2 g^{-1}$ for the calcined powder, indicating the development of significant porosity.

Continuous Processing

A very practical question to be answered is, if the colloids described above can be prepared in quantities or in a continuous process. To design the latter or any scaleup procedure, it is essential to establish the optimum conditions in batch experiments.

It was shown that spherical hematite particles could be generated continuously in a flow system using the parameters evaluated in the static process.[82] A much larger scale plug-flow type of a reactor, schematically illustrated in Figure 15, has been successfully used to produce colloidal yttrium basic carbonate particles over a 12-h period without a change in their modal diameter or size distribution.[83] The same material was prepared in quantities in a batch reactor.[84]

Internally Composite Multication Particles

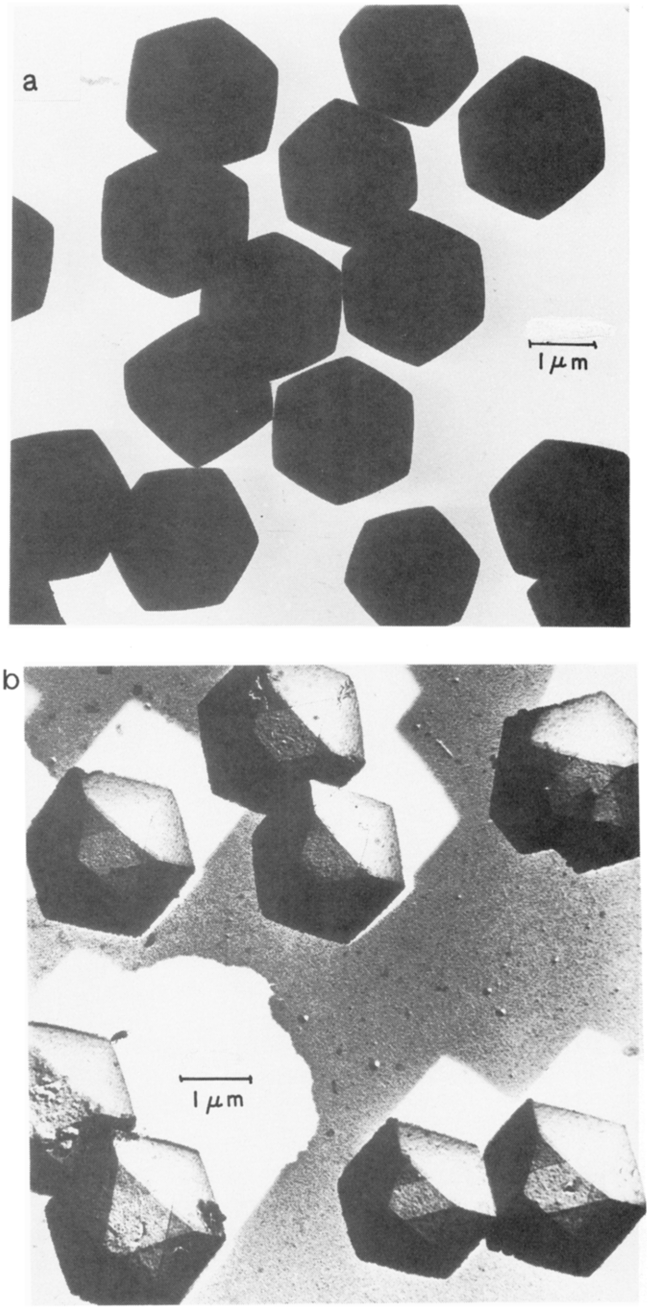

Figure 8. (a) TEM and (b) electron micrograph replica of ferric basic sulfate (alunite), $Fe_3(SO_4)_2(OH)_5{\cdot}2H_2O$, particles obtained by aging at 98 °C for 2.8 h an 8.8 × 10^{-2} mol dm^{-3} aqueous ferric sulfate solution.[48]

It was shown in previous sections that the precipitates of many sparingly soluble compounds contain more than one anion, such as in metal basic sulfates or carbonates. Precipitation from homogeneous solutions can be employed for the preparation of uniform colloidal particles containing more than one cation, although there are some important aspects of this procedure which need to be examined. To produce internally composite particles of hydrous oxides, a solution of two (or more) metal salts is aged at elevated temperatures in order to simultaneously hydrolyze all cations. Thus, spherical particles of narrow size distributions could be obtained in aqueous solutions with combinations of Cu(II)–Y(III),[85] Cu(II)–La(III),[85] Al(III)–Y(III),[86] Y(III)–Ce(III),[53] and Zr(IV)–Y(III)[59] salts.

Owing to different rates of deprotonation of hydrated metal ions, it is expected the internal composition of particles formed in solutions of more than one salt, to vary with their growth. To investigate this effect, the process

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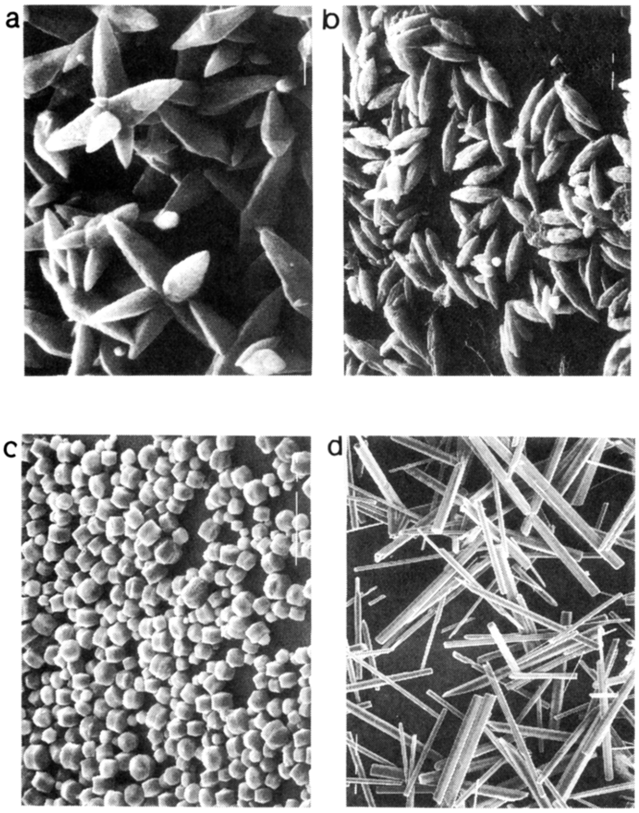

Figure 9. SEM of ZnO (zincite) particles obtained by aging the following solutions: (a) 5.0×10^{-3} mol dm^{-3} $Zn(NO_3)_2$ and 1.9×10^{-2} mol dm^{-3} NH_4OH (pH 8.8) at 90 °C for 3 h; (b) 1.0×10^{-4} mol dm^{-3} $Zn(NO_3)_2$, and 3.2×10^{-4} mol dm^{-3} NH_4OH (pH 7.7) at 90 °C for 1 h; (c) 3.2×10^{-3} mol dm^{-3} $Zn(NO_3)_2$ and 1.0×10^{-1} mol dm^{-3} triethanolamine (TEA, pH 8.9) at 90 °C for 1 h; and (d) 4.0×10^{-2} mol dm^{-3} $Zn(NO_3)_2$, 2.0×10^{-1} mol dm^{-3} TEA, and 1.2 mol dm^{-3} NaOH (pH 12.1) at 150 °C for 2 h. Longer bar in (a) and (b) equals 1 μm, whereas the longest bar in (c) and (d) equals 10 μm.[49]

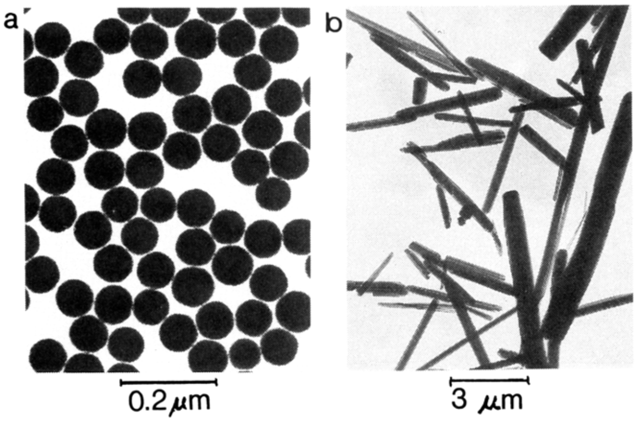

Figure 10. TEM of $Y(OH)CO_3$ particles obtained by aging solutions of (a) 1.6×10^{-2} mol dm^{-3} $Y(NO_3)_3$ and 3.3×10^{-1} mol dm^{-3} urea at 85 °C for 3 h and (b) 3.0×10^{-2} mol dm^{-3} YCl_3 and 3.3 mol dm^{-3} urea at 110 °C for 20 h.[53]

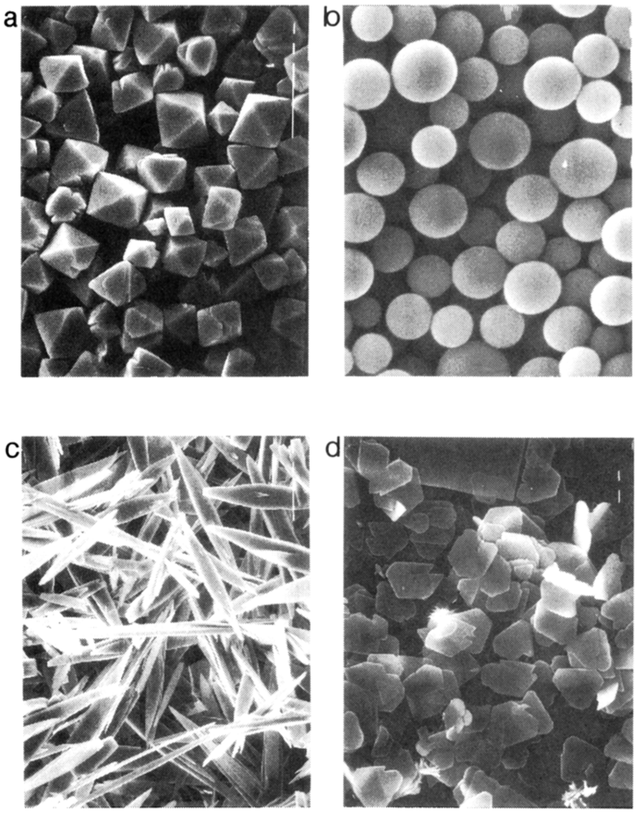

Figure 11. SEM of particles obtained by aging at 90 °C the following solutions: (a) 2.0×10^{-3} mol dm^{-3} $CuCl_2$ and 4.0×10^{-1} mol dm^{-3} urea for 120 min; (b) 8.0×10^{-3} mol dm^{-3} $Cu(NO_3)_2$ and 2.0×10^{-1} mol dm^{-3} urea for 100 min; (c) 6.0×10^{-3} mol dm^{-3} $CuSO_4$, and 2.0×10^{-2} mol dm^{-3} urea for 100 min; and (d) 1.2×10^{-3} mol dm^{-3} $CuSO_4$ and 3.0×10^{-1} mol dm^{-3} urea for 60 min.[55]

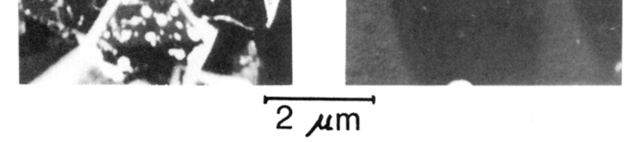

Figure 12. TEM replicas of copper(I) oxide particles obtained by rapidly heating to 95 °C and then immediately cooling down in ice-water bath copper(II) tartrate (Fehling) solutions at pH ~ 12 in the presence of 1.3×10^{-3} mol dm^{-3} glucose.[67] Concentrations of the Cu(II) complex: (a) 6.9×10^{-3} mol dm^{-3} and (b) 2.8×10^{-3} mol dm^{-3}.

was allowed to proceed for different lengths of time, the system was then quenched, and the solids were analyzed for the content in constituent metals. It was shown for Cu/Y, Cu/La, and Al/Y hydrous oxides that the molar ratio of cations changed with the size of the particles so generated, being different from that in the original solution.[85] Obviously, the internal chemical composition of such composites varied from the center to the periphery, as illustrated on the example of the Al/Y mixed hydrous oxide system (Figure 16).[86] Once the reaction was brought to completion the overall content of the solids in terms of the ratios of incorporated cations equalled that in the starting solution.

If the two constitutional oxides, prepared separately, precipitate as amorphous spheres, the mixed oxides are of the same shape and structure. On calcination at elevated temperatures the composite solids crystallize to yield stoichiometrically defined compounds, while preserving the spherical morphology.

Solids of mixed metal non-oxides can also be obtained by coprecipitation. Figure 17 is a SEM of $PbS \cdot xCdS$

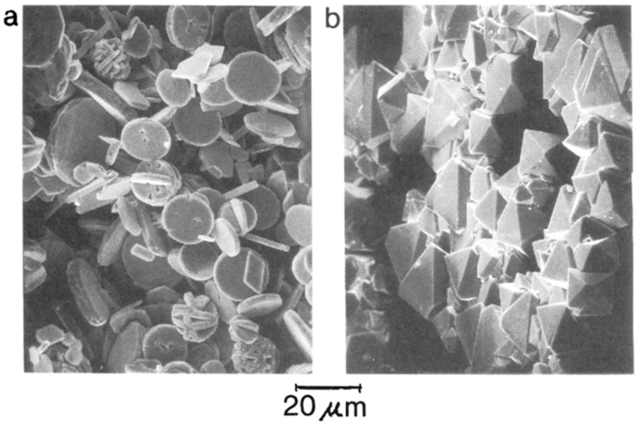

Figure 13. SEM of (a) hematite (α-Fe_2O_3) particles[68] obtained by aging at 250 °C for 1 h a solution 4.0×10^{-2} mol dm^{-3} $Fe(NO_3)_3$, 2×10^{-1} mol dm^{-3} triethanolamine (TEA), 1.2 mol dm^{-3} NaOH, and 5×10^{-1} mol dm^{-3} H_2O_2. (b) Co_3O_4 particles[69] obtained by aging at 250 °C for 3 h a solution 4×10^{-2} mol dm^{-3} $Co(NO_3)_2$, 2×10^{-1} mol dm^{-3} *N*-(2-hydroxyethyl)ethylenediaminetriacetate (HEDTA), 1.2 mol dm^{-3} NaOH, and 5×10^{-1} mol dm^{-3} H_2O_2.

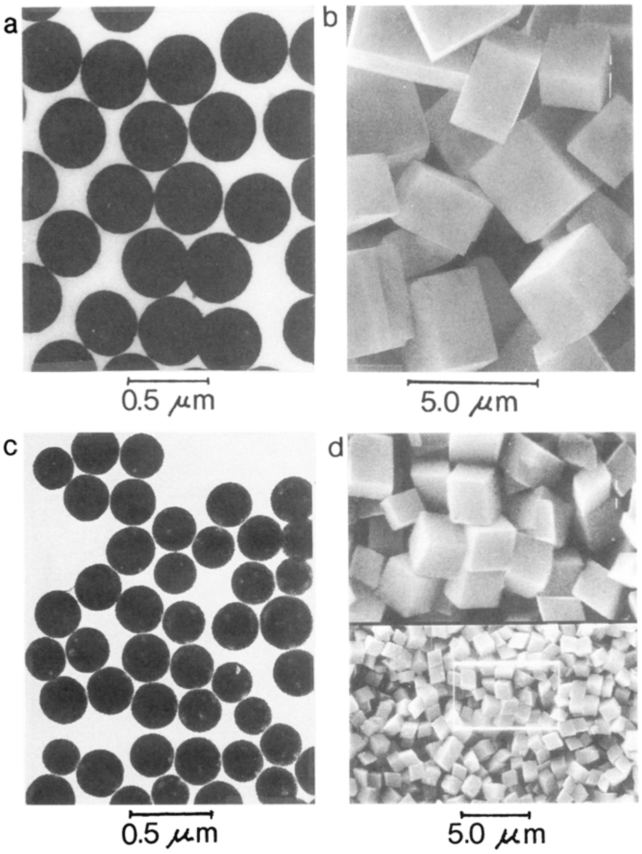

Figure 14. (a) TEM of zinc sulfide particles obtained by aging at 26 °C for 5 h a solution of 2×10^{-2} mol dm^{-3} $Zn(NO_3)_2$, 6.2×10^{-2} mol dm^{-1} HNO_3, and 1.1×10^{-1} thioacetamide (TAA) and then continued aging it at 60 °C for 6 h.[72] (b) SEM of lead sulfide particles obtained by first preparing a "seed sol" by keeping at 26 °C for 21 h a solution of 1.2×10^{-3} mol dm^{-3} $Pb(NO_3)_2$, 2.4×10^{-1} mol dm^{-3} HNO_3, and 5.0×10^{-3} mol dm^{-3} TAA, to which was then added 1.25×10^{-3} mol dm^{-3} TAA and continued aging for 1 h.[73] (c) TEM of manganese(II) phosphate particles obtained by aging at 80 °C for 3 h a solution of 5.0×10^{-3} mol dm^{-3} $MnSO_4$, 5.0×10^{-3} NaH_2PO_4, 1 mol dm^{-3} urea, and 1.0×10^{-2} mol dm^{-3} sodium dodecyl sulfate (SDS).[80] (d) SEM of $CdCO_3$ particles obtained by mixing equal volumes solution of 10 mol dm^{-3} urea preheated at 80 °C for 24 h and 2.0×10^{-3} mol dm^{-3} $CdCl_2$.[81]

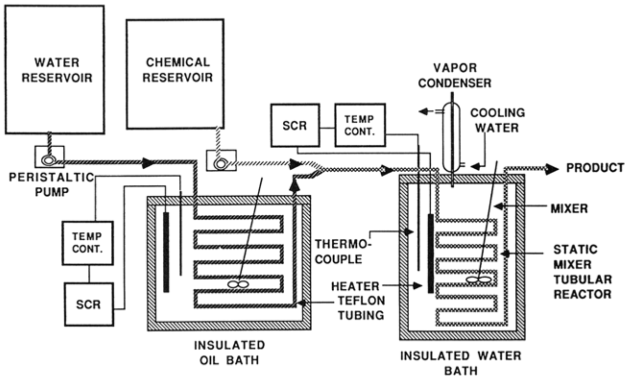

Figure 15. Schematic presentation of the apparatus for the continuous flow precipitation of the monodispersed yttrium basic carbonate.[83]

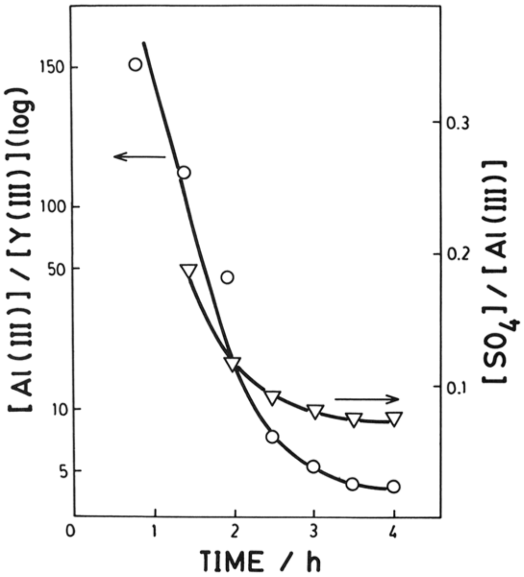

Figure 16. Changes of molar ratios [Al(III)]/[Y(III)] and [SO_4]/[Al(III)] in solids obtained by aging at 90 °C for increasing periods of time solutions consisting of 3.8×10^{-3} mol dm^{-3} $Al(NO_3)_3$, 2.2×10^{-3} mol dm^{-3} $AlNH_4(SO_4)_2$, 2.0×10^{-3} mol dm^{-3} $Y(NO_3)_3$, 0.5 mol dm^{-3} urea, 5.0×10^{-3} mol dm^{-3} HNO_3, and 2 wt % poly(vinylpyrrolidone) (PVP).[86]

particles so prepared.[73] It is interesting that in this case a "hybrid" shape is observed, because PbS alone is prismatic (Figure 14b), while cadmium sulfide appears in perfectly spherical shape.[71] The X-ray diffraction pattern of the internally composite sulfides showed major lines characteristics of both crystals, i.e., galena and greenockite (CdS).

While the above examples refer to compounds of mixed but variable compositions, the procedures have been developed which yield particles with two or more cations of well-defined stoichiometry, such as different perovskites or ferrites.

Several titanates and niobates were obtained by reactions of metal chelates in the presence of an oxidizing agent. In most cases amorphous spherical particles of narrow size distribution were precipitated, which crystallized on calcination at elevated temperatures. The electron micrograph in Figure 18a is of barium titanate prepared by simultaneous decomposition of a titanium(IV) alkoxide and a Ba–EDTA complex in an aqueous solution containing H_2O_2.[87] Using analogous procedures, lead titanate[88] and niobates of potassium,[89] magnesium,[89]

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(88) Kim, M. J.; Matijević, E. *Chem. Mater.* **1989**, *1*, 363.
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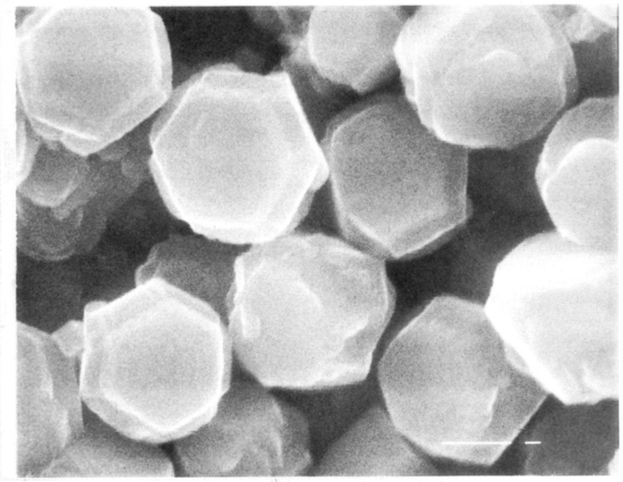

Figure 17. SEM of mixed PbS·xCdS particles prepared by the addition of 0.50 cm^3 of 4.3 × 10^{-3} mol dm^{-3} $Cd(NO_3)_2$ and 1.00 cm^3 of 2.1 × 10^{-2} mol dm^{-3} $Pb(NO_3)_2$ to 20 cm^3 of a lead sulfide "seed" sol (obtained by aging a solution of 1.2 × 10^{-3} mol dm^{-3} in $Pb(NO_3)_2$, 5.0 × 10^{-3} mol dm^{-3} in TAA and 2.4 × 10^{-3} mol dm^{-3} in HNO_3 at 26 °C for 21 h) and allowing the dispersion to age at 80 °C for 30 min.[73] The longer bar equals 1 μm.

and lead[90] were synthesized. In the latter case, depending on conditions, either spherical or cubic particles (e.g., Figure 18b) were precipitated. The exact chemical composition of these compounds depended somewhat on the conditions of precipitation.

Uniform colloidal magnetite[91] was prepared by first precipitating iron(II) hydroxide and subsequent aging in the presence of a mild oxidizing agent. Various ferrites were obtained using the same procedure by replacing a fraction of ferrous ions with other divalent metals, such as nickel,[92] cobalt,[93] (or both),[94] barium,[95] and strontium.[96] Figure 18c illustrates spherical particles of nickel ferrite,[92] while hexagonal platelets in Figure 18d are of barium ferrite.[95] Partial substitution of ferric ions by Cr(III) yielded uniform chromite particles.[97]

Finally, Figure 19 shows a recently prepared powder of $NaMgF_3$ which has the orthorhombic structure of neighborite.[98]

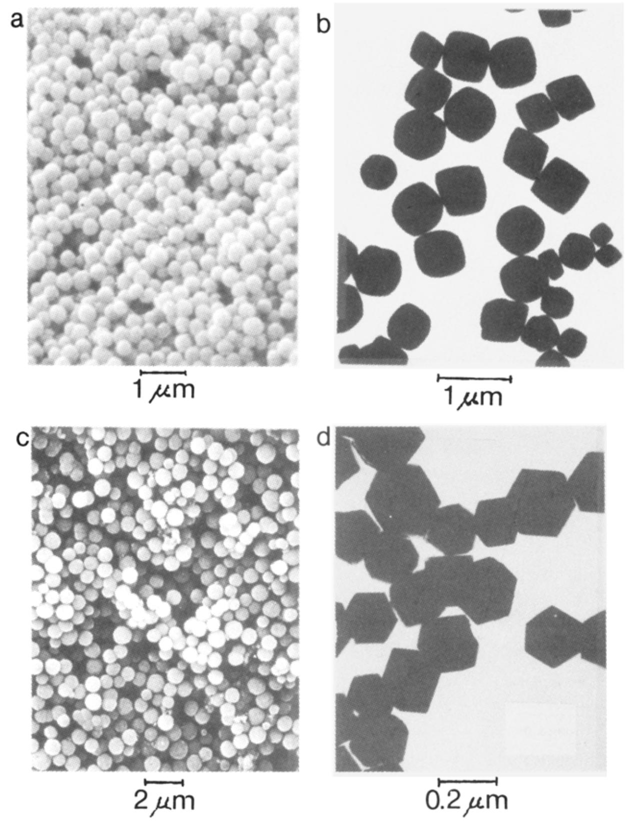

Figure 18. (a) SEM of barium titanate particles obtained by aging at 60 °C for 2 h a solution of the following composition: titanium(IV) isopropoxide, [Ti(i-Opr)$_4$] = 5.0 × 10^{-3} mol dm^{-3} [Na_2H_2EDTA] = 1.0 × 10^{-2} mol dm^{-3}, [$BaCl_2$] = 5.0 × 10^{-3} mol dm^{-3}, and [H_2O_2] = 0.38 mol dm^{-3}; pH was adjusted to 9.9 by addition of NH_3.[87] (b) TEM of lead niobate particles obtained by aging at 50 °C for 4 h a solution of 8.0 × 10^{-3} mol dm^{-3} $Pb(NO_3)_2$, 2.0 × 10^{-3} mol dm^{-3} $NbCl_5$, and 1.0 × 10^{-2} mol dm^{-3} Na_2HNTA in the presence of H_2O_2.[90] (c) SEM of nickel ferrite particles obtained on aging at 90 °C for 4 h coprecipitated ferrous and nickel hydroxide gels in the ratio [$Ni(OH)_2$]/[$Fe(OH)_2$] = 0.5 in the presence of excess 6.0 × 10^{-2} mol dm^{-3} $FeSO_4$ and 2.0 × 10^{-1} mol dm^{-3} $NaNO_3$.[92] (d) TEM of barium ferrite particles obtained by aging at 90 °C a system consisting of 1.25 × 10^{-1} mol dm^{-3} $FeCl_2$, 1.5 × 10^{-1} mol dm^{-3} KOH, 2.0 × 10^{-1} mol dm^{-3} KNO_3, and 1.0 × 10^{-2} mol dm^{-3} $Ba(NO_3)_2$ as described in ref 95.

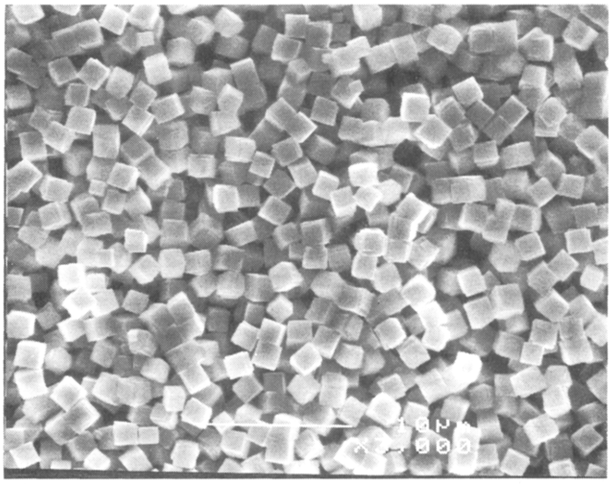

Figure 19. SEM of neighborite, $NaMgF_3$, particles obtained by aging at 80 °C for 3 h a solution of 1.6 × 10^{-1} mol dm^{-3} NaF and 4.0 × 10^{-2} mol dm^{-3} $MgCl_2$.[98]

Coated and Hollow Particles

There are several reasons that make it useful to cover core materials with shells of different chemical composition. One is to change physical (optical, magnetic, conductive, etc.) or chemical properties of a dispersion by the choice of the coating material. Furthermore, when a required particle shape is impossible to achieve by direct synthesis, cores of the desired morphology can be coated with another compound necessary for a given application.

Shells of different thickness on various substrates can be produced either by deposition of tiny precursor particles or by direct precipitation of a homogeneous layer on the core materials. In the first case one deals essentially with heterocoagulation, while the second process is dependent on the precipitation properties of the coating material and on the proper ratio of the amount of cores to the

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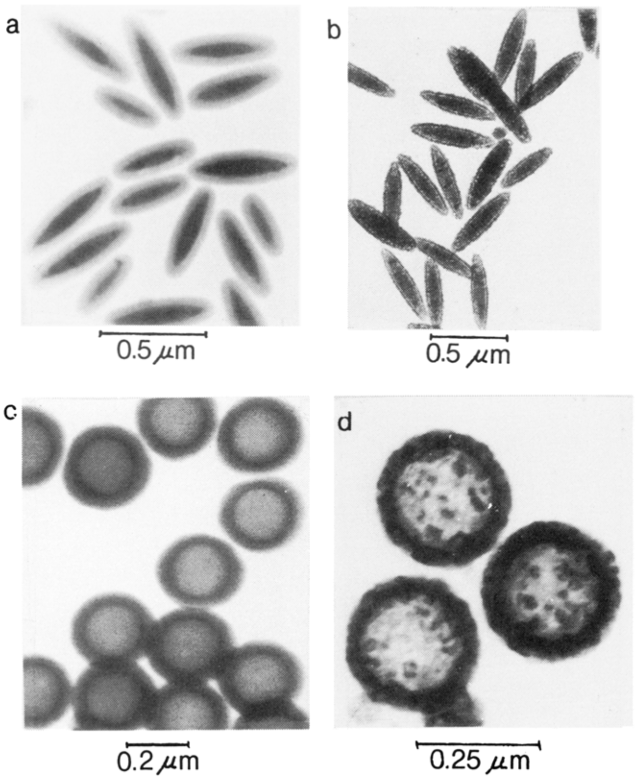

Figure 20. (a) TEM of hematite (α-Fe_2O_3) particles coated with silica by aging at 40 °C for 18 h a dispersion of 72.7 mg dm^{-3} cores in 2-propanol containing 0.45 mol dm^{-3} NH_3, 3.05 mol dm^{-3} H_2O, and 4.0×10^{-4} mol dm^{-3} tetraethyl orthosilicate (TEOS).[103] (b) TEM of hematite particles coated with zirconium (hydrous) oxide by aging at 70 °C for 2 h an aqueous dispersion of 600 mg dm^{-3} cores containing 5.0×10^{-3} mol dm^{-3} zirconium sulfate, 5 vol % formamide, and 0.5 wt % poly(vinylpyrrolidone) (PVP).[102] (c) TEM of polystyrene latex coated with yttrium basic carbonate by aging at 90 °C for 2 h a dispersion of 100 mg dm^{-3} PS latex containing 5.0×10^{-3} mol dm^{-3} $Y(NO_3)_3$, 1.8×10^{-3} mol dm^{-3} urea, and 1.2 wt % PVP.[105] (d) TEM of hollow yttria particles obtained by calcining at 800 °C for 3 h coated particles shown in Figure 20c.[106]

concentration of the electrolyte solution which produces the shell. When the coating is formed by the deposition (heterocoagulation) mechanism, the optimum conditions are determined by the charge and other characteristics of both solid reactants, as expected in the particle adhesion process.

Many different core materials, such as hematite, chromia, and titania, have been coated with the same shell (aluminum hydroxide),[99] or the same core material (e.g., hematite) was covered with layers of different chemical composition, including yttria,[100] chromium (hydrous) oxide,[101] zirconium (hydrous) oxide,[102] or silica.[103]

Electron micrographs (Figures 20a and b) of ellipsoidal hematite (α-Fe_2O_3) cores coated with silica[103] and zirconia,[102] respectively, show uniform shells on each particle. Chemical characteristics of such solids are essentially determined by the composition of the outer layer. As an example Figure 21 displays the differential thermal analysis (DTA) data for hematite and chromium hydroxide powders when precipitated alone, as well as of hematite cores coated with chromium hydroxide; obviously the last two curves show the same behavior.[101]

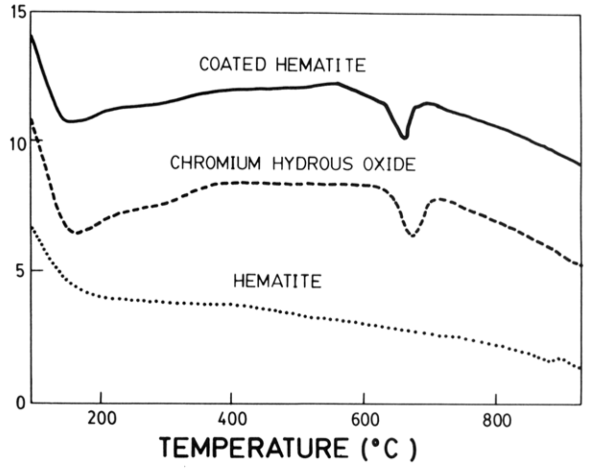

Figure 21. Differential thermal analysis data for hematite, chromium hydroxide, and hematite particles coated with chromium hydroxide.[101]

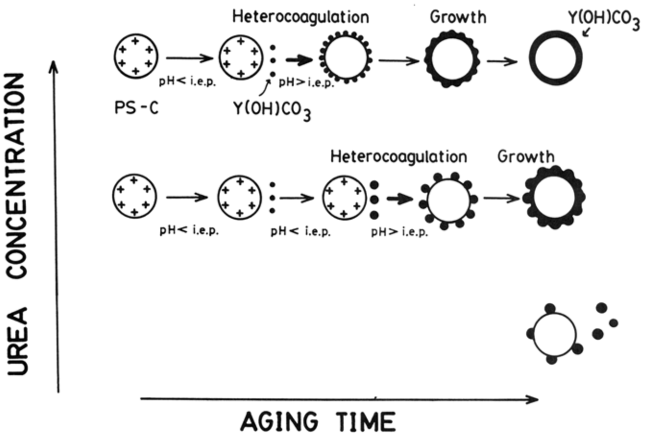

Figure 22. Schematic presentation of the coating mechanism of positively charged polystyrene latex by yttrium basic carbonate at different urea concentrations as a function of aging time at 90 °C.[105]

Inorganic shells can also be produced on organic cores, as demonstrated with zirconium (hydrous) oxide[104] or yttrium basic carbonate[105] on polystyrene (PS) latex. The latter particles are illustrated in Figure 20c. The outer layer does not appear smoth under all conditions; the PS cores can be either partially covered or mixed dispersions may develop. In all these cases the coating is produced by the heterocoagulation mechanisms; thus, the size and the charge of the coating particles, precipitated in the presence of the latex, must control the processes involved, as schematically shown in Figure 22.[105] At first, positively charged finely dispersed yttrium basic carbonate is formed. With aging, urea decomposes and the pH of the system rises, eventually exceeding the isoelectric point (iep) of $Y(OH)CO_3$, which then interacts with the positively charged latex. At high urea concentrations this charge reversal occurs early while the $Y(OH)CO_3$ particles are still very small, producing a smooth coating on deposition on the latex. At lower urea contents the pH change is slower and the particles of the coating material grow to a considerably larger size before charge reversal takes place, resulting either in rough shells or in mixed dispersions.[105]

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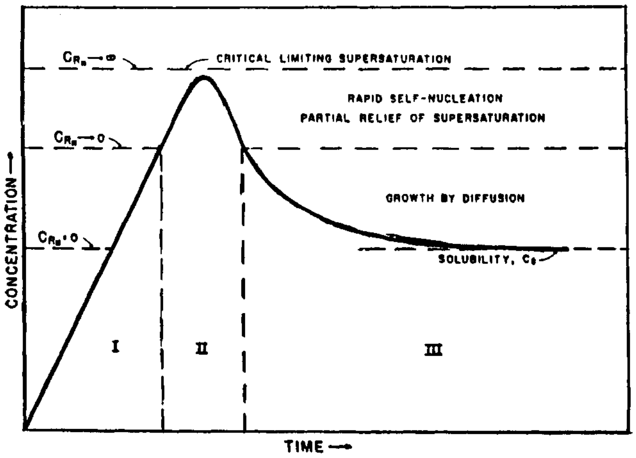

Figure 23. Schematic representation of concentration of molecularly dissolved sulfur before and after nucleation as function of time (LaMer).[16,107]

One particular aspect of the polymer cores covered with inorganic layers worth mentioning is their usefulness in the preparation of hollow particles. On careful calcination of such composite materials, the organic matter can be burned off, leaving behind the spherical shells with void centers, as illustrated in Figure 20d on the example of yttria.[106] In an analogous manner hollow zirconia particles have been obtained by heating latex particles coated with zirconium (hydrous) oxide.[104]

Mechanisms of the Formation of Uniform Particles

The foregoing examples, selected from a large number of reported "monodispersed" colloids, clearly demonstrate that precipitation processes in homogeneous solutions can be controlled to yield uniform particles of different chemical composition, structure, shape, and size. The fact that all these characteristics can be altered using the same reactant solutions points to the complexity of the processes involved, which are sometimes affected by a small change in experimental conditions.

Physical Aspects. In consideration of the mechanisms of the formation of well-defined particles, it is necessary to distinguish between two stages, which often overlap; i.e., the formation of nuclei in a homogeneous environment and their subsequent growth to particles of larger size. Most of the original concepts in the design of the experiments for the preparation of "monodispersed" colloids were based on the LaMer model,[107] which was developed to explain the formation of uniform spherical sulfur particles.[108] LaMer's schematic diagram, the variations of which have been reproduced countless times, is given in Figure 23, including the original legend.[107] In essence, this model implies that monodispersed particles are formed, when the process in a homogeneous solution is conducted in a kinetically controlled manner, so that the concentrations of constituent species reach critical supersaturation, resulting in a short single burst of nuclei. The latter are then allowed to grow uniformly by diffusion of solutes to the so produced dispersed solids. The obvious appeal of this simplistic mechanism was in—what appeared to be—reasonable assumptions, especially since many dispersions prepared by homogeneous precipitation yielded uniform spheres. Recently, it has been amply demonstrated that LaMer's approach is applicable in a limited number of cases and often only to the initial stages of the precipitation process.

In describing the mechanisms of the formation of monodispersed colloids, it is certainly necessary to consider the nucleation and particle growth stages, from both the chemical and physical points of view. While physical aspects are not simple, they involve less specificity than chemical ones, which differ in each and every case.

The recognition of the limitations of the LaMer model came through a number of experimental findings that contradicted it. For example, it has been proven in several cases for nucleation to be an ongoing process, yet still "monodispersed" colloids were generated. It was also found that many uniform *spheres*, prepared by homogeneous precipitation, exhibited X-ray spectra of well-known minerals, which could not be explained by diffusional growth alone.

The situation will obviously differ, if constituent species are simple ions, such as in the formation of silver halides, where the interactions mostly take place between the silver cation and the halide anion, from processes in solutions of diverse complexes. Thus, it is essential to distinguish between systems produced in different kinds of media. In all instances the precipitation can only take place when the concentration of particle forming solutes exceeds their solubility.

With respect to the nucleation stage, the concept of a short lived burst has been shown inadequate both in solutions of simple or complex species. For example, Sugimoto developed a theory of the nucleation process for monodispersed sparingly soluble colloidal particles in an open system, which is based on the assumption that stable nuclei are produced through a kind of Ostwald ripening of originally formed unstable nuclei.[109] This model explained many aspects of the formation of well-defined silver bromide particles.

A continuous nucleation/aggregation process has been also introduced to explain the formation of uniform spherical silica particles by the hydrolysis of TEOS[110–112] originally developed by Stöber et al.[32]

Note added in proof: After this review was accepted for publication, a comprehensive study on this subject was published by A. Van Blaardeen, J. Van Geest and A. Vrij (*J. Colloid Interface Sci.* **1992**, *154*, 481). These authors have shown that the aggregation mechanism proposed by Zukoski et al. is based on inadequate interpretation of electron microscope observations. Instead, a hydrolysis-driven polymerization mechanism is suggested.

The mounting evidence that the initially formed tiny dispersed solids often coagulate to uniform larger particles, both of spherical and of other shapes (cubes, prisms, rods, etc.), indicates the inadequacy of the assumed growth mechanism by the diffusion of the solutes onto preformed nuclei. The internal aggregated state of the final products

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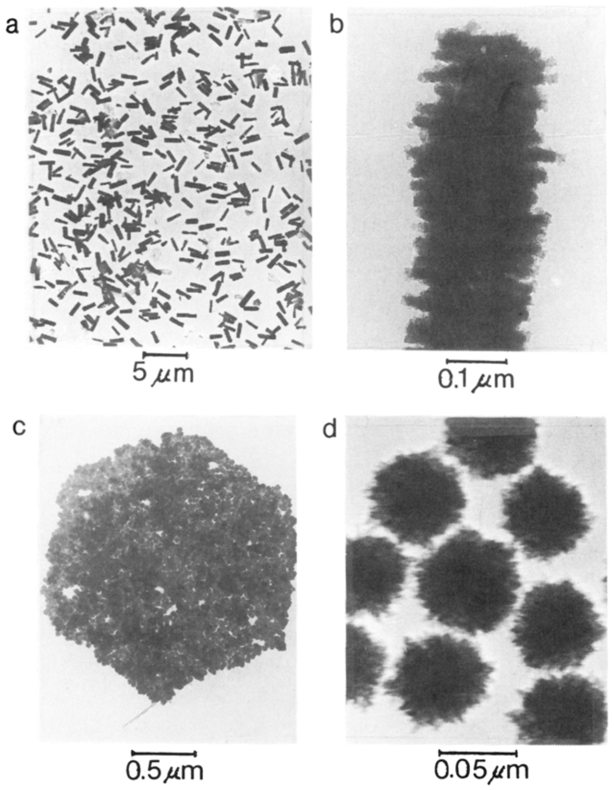

Figure 24. (a) TEM of rodlike cerium basic sulfate particles obtained by aging at 90 °C for 12 h a solution of 2.5×10^{-3} mol dm^{-3} $Ce(SO_4)_2$, 1.0×10^{-2} mol dm^{-3} H_2SO_4, and 4.0×10^{-1} mol dm^{-3} Na_2SO_4;[38] (b) similar particles as (a) at higher magnification; (c) TEM of hexagonal particle obtained by aging under the same conditions a solution of 1.5×10^{-2} mol dm^{-3} $(NH_4)_2Ce(NO_3)_6$, 6.4×10^{-2} mol dm^{-3} H_2SO_4, 1.6×10^{-1} mol dm^{-3} Na_2SO_4, pH 1.1;[38] and (d) TEM of SnO_2 (cassiterite) particles obtained by aging at 100 °C for 2 h a solution of 3.0×10^{-3} mol dm^{-3} $SnCl_4$ and 3.0×10^{-1} mol dm^{-3} HCl.[114]

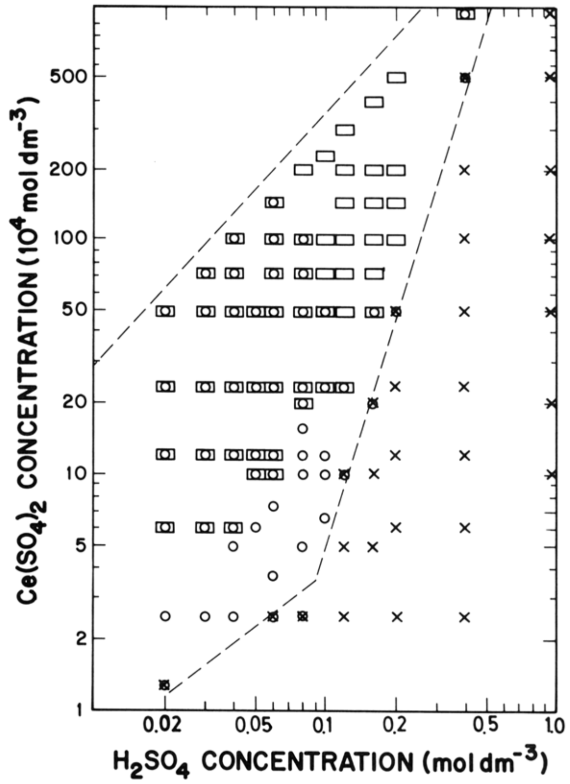

Figure 25. Precipitation domain for solutions containing different concentrations of $Ce(SO_4)_2$ and H_2SO_4 aged at 90 °C for 12 h. Symbols designate the shape of the particles: ○, spheres (Figure 5c); □, rods (Figure 24a); ⊡, rods mixed with spheres; ⊗, a very small amount of spheres; ×, no particle formation.[38]

can be visualized in some cases by high-resolution electron microscopy, while in some other cases, where perfectly smooth spheres are produced, it can be ascertained by low-angle X-ray scattering and other techniques, such as infrared analysis, based on the average dielectric constant (TADC) approach.[113]

The composite nature of colloidal particles is exemplified by the TEM of the dispersion of rodlike cerium basic sulfate (Figure 24a), which at higher magnification clearly exhibits lamellar structure (Figure 24b).[38] Hexagonal platelets (Figure 24c) obtained in solutions of $(NH_4)_2Ce(NO_3)_6$ are obviously built up of tiny spherical precursors, not evident at a low magnification. Spherical particles of CeO_2 shown in Figure 5c displayed four major X-ray lines of the face centered cubic CeO_2, yet the time-resolved electron microscopy of these dispersions (not reproduced here) nicely demonstrates the aggregation mechanism.[38] Finally, Figure 24d of colloidal SnO_2, the X-ray diffraction pattern of which is characteristic of mineral cassiterite, shows obvious internal substructure.[114] Similarly, rodlike SnO_2[115] and ellipsoidal hematite (α-Fe_2O_3) particles were identified as aggregates of fiber-type precursors.[116]

The recognition that some larger colloidal particles are made up of smaller subunits is not new; such information has been reported for several, but polydisperse, solids.[108,117–119] The newer data show that the aggregation mechanism prevails in a large number of systems leading to the formation of monodispersed particles. There are still questions that need clarification. For example, some of the composite spheres show distinct roughness, while some others have electron-microscopically perfectly smooth surface. Furthermore, it is easily understood that small particles will tend to aggregate, particularly if their surface charge is weak or if the ionic strength of the dispersion is high. The quantitative explanation of a process by which a huge number of subunits aggregates into *identical* large particles has not been developed as yet. It is also not clear why in some instances the final particles are spherical and in others they appear in different geometric forms, yet of the same chemical composition. In summary, the present evidence on a substantial number of "monodispersed" colloids indicates that the nucleation process needs not be "instantaneous" and that the subsequent growth is mainly due to the aggregation of small precursor particles into colloids of different morphologies.

Chemical Aspects. The essence of the chemical processes and especially the importance of the nature and the kinetics of the formation of various solute complexes in defining the properties of the resulting colloidal dispersions have been sufficiently substantiated in this review. Some of the major results are summarized below.

Figure 25 displays the precipitation domain in $Ce(SO_4)_2$–

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H_2SO_4 solutions,[38] which demonstrates the effect of *reactant concentrations* alone on the chemical composition and morphology of the resulting particles, which were shown in Figures 5c and 24a.

Zinc oxide of zincite structure, but of different particle shapes (Figure 9), was produced by changing the *liquid environment*, i.e., by using different weak bases needed to raise the pH.[49]

As stated before, the *effect of anions* on the nature of the precipitated particles is of particular significance. For example, by varying the HCl content in $FeCl_3$ solutions and the aging temperature and time, colloidal hematite (α-Fe_2O_3) of different morphologies (spheres, cubes, rods, ellipsoids, etc.) is obtained (Figure 7),[39] but under somewhat different conditions needle-type akageneite (β-FeOOH) dispersions precipitate. The addition of small amounts of phosphate ions to acidified $FeCl_3$ solutions produces exceedingly uniform ellipsoidal hematite particles of different axial ratios (Figure 6), although no phosphate ions can be detected in the final products. When the amount of this anion is increased, ferric phosphate particles of spherical and other shapes are formed.[77] Solutions containing $FeCl_3$ and NaH_2PO_2 in different concentrations aged at 245 °C yield dispersions of a variety of compositions and shapes.[120] Finally, in the presence of sulfate ions, well-defined crystalline alunites are generated (Figure 8).[48]

The effect of anions is equally pronounced when precipitation is carried out in the presence of urea, as exemplified with copper(II) salts. Solutions of $Cu(NO_3)_2$, $CuCl_2$, or $CuSO_4$ yield particles of varying morphologies, associated with their different chemical composition, which is in some cases affected by the generated carbonate ion (Figure 11).[54]

To elucidate the chemical mechanisms responsible for the precipitation of particles of given characteristics, it is necessary to establish the natures of all solute complexes and to follow the changes in their concentrations under conditions that yield a specific product. Only then it should be possible to relate different properties of the solids to the chemical speciation in the solution in which they are precipitated. It is unfortunate that little information on the essential solute complexation is available in the literature, especially at elevated temperatures of importance in most preparation procedures. In some instances the speciation was experimentally established to fit exactly the conditions of the particle formation. Such an analysis was carried out with ferric sulfate solutions, and Table I lists the concentrations of all species at the pH of interest at three different temperatures.[121]

It is evident that the $FeSO_4^+$ complex is dominant in all cases, while $FeOH^{2+}$ is the most abundant hydrolysis product at lower temperatures. With rising temperature, the relative concentration of $Fe(OH)_2^+$ increases and at 80 °C this species exceeds in content the primary hydrolysis product, $FeOH^{2+}$.

Table I. Molar Concentrations of Various Complexes Present at Different Temperatures in a Solution Initially 0.18 mol dm^{-3} in $Fe(NO_3)_3$ and 0.53 mol dm^{-3} in Na_2SO_4 at pH 1.7

	temperature, °C		
species	25	55	80
Fe^{3+}	1.78×10^{-2}	8.89×10^{-3}	3.30×10^{-3}
$FeOH^{2+}$	1.07×10^{-3}	1.60×10^{-3}	1.46×10^{-3}
$Fe(OH)_2^+$	8.9×10^{-5}	6.4×10^{-4}	5.23×10^{-3}
$Fe_2(OH)_2^{4+}$	4.8×10^{-4}	4.0×10^{-4}	1.1×10^{-4}
$FeSO_4^+$	1.58×10^{-1}	1.66×10^{-1}	1.69×10^{-1}
$FeHSO_4^{2+}$	2.57×10^{-3}	2.25×10^{-3}	8.0×10^{-4}
SO_4^{2-}	1.06×10^{-1}	7.60×10^{-2}	5.00×10^{-2}
HSO_4^-	2.91×10^{-2}	6.32×10^{-2}	1.22×10^{-1}
$NaSO_4^-$	2.35×10^{-1}	2.23×10^{-1}	1.87×10^{-1}

It was established experimentally that at room temperature only alunite type colloidal particles of hexagonal crystal symmetry are formed, having the chemical composition $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$. Considering data in Table I, the following overall reaction is suggested:

$$FeOH^{2+} + 2FeSO_4^+ + 6H_2O \rightarrow \underset{\text{hexagonal}}{Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O} + 4H^+$$

At the higher temperature, the increasing amount of the $Fe(OH)_2^+$ complex explains the observed simultaneous appearance of hexagonal and monoclinic alunite particles.[48] The latter could form according to[121]

$$3Fe(OH)_2^+ + FeSO_4^+ + 4H_2O \rightarrow \underset{\text{monoclinic}}{Fe_4(SO_4)(OH)_{10}} + 4H^+$$

An analogous comprehensive chemical analysis of the precipitation process was carried out in order to explain the formation of amorphous $Cr(OH)_3$ particles.[122]

The ultimate aim in the studies of chemical mechanisms in the precipitation from homogeneous solutions is to develop some general principles, that would make predictable the processes leading to the formation of uniform particles. The most serious effort in this direction has been made by Livage and associates, who introduced a concept that helps explain the formation of different metal (hydrous) oxides, based on electronegativity data, designated as the "partial charge model" (PCM).[123,124] Since these solids represent the final stage of the hydrolysis process, it is essential to be able to predict the deprotonation reactions of a hydrated metal ion in aqueous solutions, which this model is capable of doing.[125]

The same concept has been extended to complexes that include different anions in the hydrolyzed solutes, adding to the understanding of the effects of such precursors on the nature of the precipitated solids. Specifically, it is possible to predict the pH region over which an anion can be incorporated into a hydrolyzed metal cation. For example, the model explains why the hydrolysis of $TiCl_4$ in the presence of HCl or HNO_3 leads to the formation of TiO_2 of rutile structure, whereas H_2SO_4 yields anatase. In the latter case, the complexation by sulfate ions is responsible for the "cis" chain conformation of TiO_6 octahedra characteristic of anatase.[123] While the approach by Livage has rationalized some of the experimental findings, it is only useful in explaining relatively simple

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cases. Furthermore, it is still not possible to predictably design conditions to generate a dispersion of precise properties.

One of the vexing problems of fine particle science, which has ramifications in many other areas (e.g., geology, crystallography, etc.), is related to particle morphology. It is easily recognized that amorphous particle should be spherical. Other shapes of particles can be related to the chemical composition, which may correspond to a known mineral. However, in many cases there is no rationale to explain the appearance of a given particle morphology. The predictability of a specific shape and structure is further obscured by the recognition that a great many solids are generated through the aggregation process as discussed earlier. Since some of these particles appear as well-developed crystals, sometimes of different shapes but of the same composition, their formation must be affected by the properties of the precursor subunits.

To throw some light into the problems of particle shapes, Livage and associates have focused on the precipitation in solutions of metal alkoxides, especially of Ti(IV) alkoxides. It was demonstrated that the morphology of the resulting TiO_2 solids was strongly dependent on the natures of the alkoxy groups (especially their bulkiness), which determined the molecular structure of the solute complexes. XANEX spectra indicated that primary alkoxy groups form trimers with Ti(IV) surrounded by five ligands, while secondary and tertiary alkoxide groups remain monomeric with Ti in a 4-fold coordination.[124] The latter are much more reactive, leading to polydisperse systems, while tetraethoxy–Ti(IV) yields monodispersed TiO_2 particles. Similar arguments have been developed with acetylacetonate complexes of titanium, zirconium, and cerium(IV).[126]

Concluding Remarks

While tremendous progress has been made in the preparation of a large number of "monodispersed" colloids of simple and composite natures, many problems must yet be resolved. Especially, the mechanisms of their formation by precipitation from homogeneous solutions have to be clarified, which include both nucleation and growth stages. Furthermore, general principles regarding the relationship of the complex composition of the solution to that of the generated solid phase need to be established. One of the essential aspects to be elucidated is that of particle shapes. Until now, most efforts have been directed toward the explanation of given morphologies of synthesized colloids. The next step is to develop principles which will make it possible to predict the formation of such particles. These tasks are by no means simple, and they could not have been addressed until a sufficient number of well-defined systems of given chemical, structural, and morphological characteristics became available. Since many dispersions of specific properties have been synthesized under precisely defined conditions, the chances of getting some of the answers are now more promising. The challenge can be addressed by selecting systems of distinct characteristics and then relating these to the chemical composition of the solutes involved in their formation. It is also essential to establish the natures of the nucleation and growth processes that take place in the same environments but result in different products.

It should be noted that monodispersed colloids prepared so far have been used in many studies with the purpose of relating different properties, such as optical, magnetic, conductive, etc., to the particle composition, size, and shape. Such dispersions have also been employed in the investigations of hetero(coagulation), adhesion, filtration, settling, corrosion, and other processes. Finally, well-defined colloids are finding an increasing number of applications in many areas of high technology, medicine, catalysis, etc. None of these studies of academic or practical interest could be addressed in the present review.

Acknowledgment. The results described in this review are based on the work of my many associates and graduate students whose names appear in the cited references. Their enthusiasm and efforts made the described progress in the field of fine-particle science possible. The many years of studies could not have been carried out without the financial support of several agencies, including the National Science Foundation, the U.S. Air Force, and the Electric Power Research Institute.

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