Monodispersed inorganic colloids: Achievements and problems

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Abstract – It is shown that a large number of dispersions consisting of uniform colloidal particles of different chemical compositions and shapes can be obtained by precipitation from homogeneous solutions. Recently, much emphasis has been placed on internally mixed or coated particles. Finally, hollow spherical particles of metal oxides have been produced. A number of problems that still require intensive studies are outlined.

INTRODUCTION

The importance of the so called "monodispersed" particles has been sufficiently emphasized both for academic and practical reasons. The most convenient method for the preparation of such dispersions is by the control of chemical processes in homogeneous solutions, which lead to the solid state formation. The fundamental principles for the precipitation of well defined systems are reasonably well understood, which resulted in a large number of uniform powders of different chemical compositions in a variety of particle shapes. However, with the advance of this science, new problems are encountered that need to be addressed.

STRUCTURE AND SHAPE OF PARTICLES

The predictability of the structure and of the shape of uniform particles, prepared by precipitation from homogeneous solutions, is still a major unresolved problem. In some cases solids of the same chemical composition appear in a variety of morphologies due to relatively small changes in experimental conditions, as shown with hematite (ref. 1) or zinc oxide (ref. 2), while in some other cases the change in the particle shape is associated with a different chemical composition, as exemplified by precipitation in acidified cerium(IV) sulfate (ref. 3) or yttrium chloride (ref. 4) solutions, respectively.

Anions of a given electrolyte also play a major role in determining both the structure and the morphology of fine particles. Some of these effects are illustrated in Fig. 1 with copper(II) salt solutions aged at 90 °C (ref. 5). In the presence of chloride ions amorphous, spherical particles are obtained, the stoichiometry of which corresponds to malachite (Fig. 1a), while the bipyramidal particles have the X-ray pattern characteristic of atacamite $[CuCl_2 \cdot 3Cu(OH)_2]$ (Fig. 1b). Copper(II) sulfate solutions yield brochantite $[CuSO_4 \cdot 3Cu(OH)_2]$ (Fig. 1c), whereas the platelets are identified by X-rays as posnjan-kite $[CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O]$ (Fig. 1d). It is noteworthy that in these experiments only the reactant concentrations and aging times have been varied.

The above example clearly points to the problems related to particle morphologies, which need to be resolved. Obviously, the complex chemistry of the solutions in which these solids are formed is mainly responsible for the natures of the products. Since each electrolyte yields different solute species, which depend on the reactant concentration, pH, temperature, anions present, etc., only systematic studies of the relationship of the solution composition to the resulting solids may eventually lead to some more general principles.
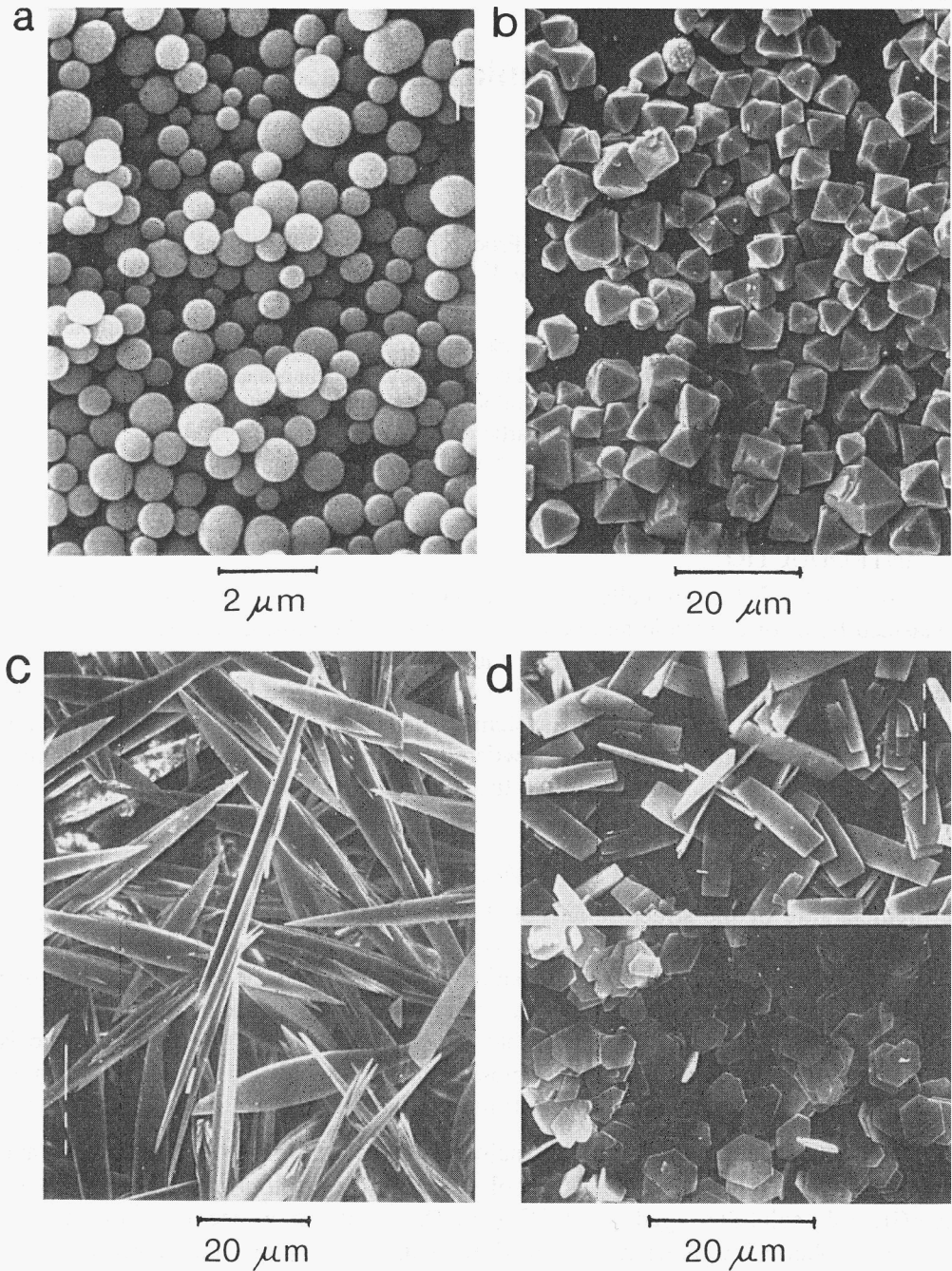
Fig. 1. Scanning electron micrographs (SEM) of particles obtained by aging at 90 °C
solutions: (a) 3×10^{-3} mol dm^{-3} in CuCl$_2$ and 2×10^{-1} mol dm^{-3} in urea (50 min);
(b) 1.2×10^{-2} mol dm^{-3} in CuCl$_2$ and 2×10^{-1} mol dm^{-3} in urea (120 min); (c) 1.5
$\times 10^{-2}$ mol dm^{-3} in CuSO$_4$ and 1.0×10^{-1} mol dm^{-3} in urea (90 min); (d) 1.2×10^{-3}
mol dm^{-3} in CuSO$_4$ and 1.5×10^{-1} mol dm^{-3} in urea (upper half) and 1.5×10^{-3} mol
dm^{-3} in CuSO$_4$ and 3×10^{-1} mol dm^{-3} in urea (lower half) (ref. 5)

Another topic of interest refers to powders consisting of spherical particles, some of
which are amorphous while others have X-ray characteristics of known minerals. It is
not difficult to understand the formation of the former. Convincing evidence shows now
that all "crystalline-like" spheres, generated directly by aging various salt solutions,
consist of a large number of subunits. Transmission electron micrographs in Fig. 2
represent two different magnification of a tin(IV) oxide powder which has been identified
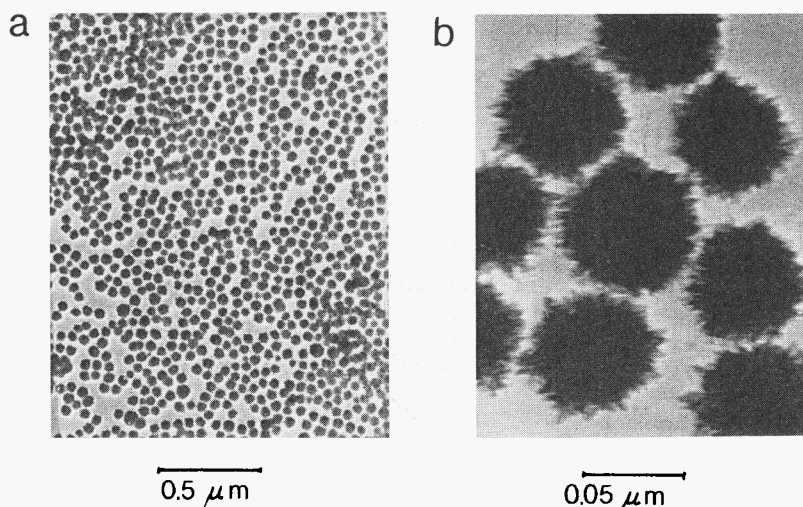
Fig. 2. (a and b) Transmission electron micrographs (TEM) of SnO_2 particles, obtained by aging for 2 h at 100 °C a solution 0.0030 mol dm^{-3} in $SnCl_4$ and 0.30 mol dm^{-3} in HCl (ref. 6)

by X-rays as cassiterite (ref. 6). It is quite apparent that the particles are composite in nature. While it is readily understood that exceedingly small precursor particles (30–50 Å) would tend to aggregate, the mechanism of the formation of much larger spheres of uniform size, containing a huge number of subunits, is still to be resolved.

The structurally composite particles are not associated with spherical shape only. Figure 3a shows rod–like particles of cerium basic sulfate which appear rather smooth. However, a much higher magnification clearly proves that these apparent "single crystals" consist of a series of lamellae (Fig. 3b) (ref. 3).
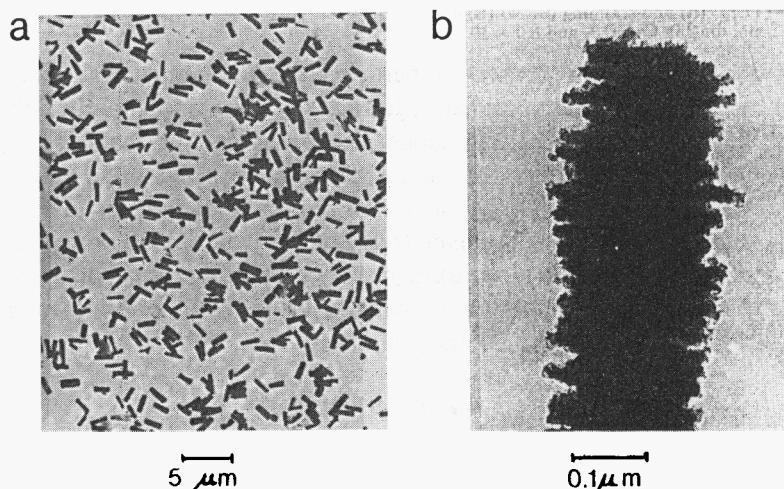

Fig. 3. TEM of rod–like particles obtained by aging at 90 °C for 12 h the following solutions: (a) 2.5×10^{-3} mol dm^{-3} in $Ce(SO_4)_2$, 1.0×10^{-2} mol dm^{-3} in H_2SO_4, and 0.4 mol dm^{-3} in Na_2SO_4; (b) 4.5×10^{-3} mol dm^{-3} in $Ce(SO_4)_2$, 2.5×10^{-2} mol dm^{-3} in H_2SO_4, and 0.45 mol dm^{-3} in Na_2SO_4 (ref. 3)

COLLOIDAL PARTICLES OF MIXED OXIDES

It has been demonstrated that spherical particles containing more than one metal can be precipitated from electrolyte solutions of two different salts (ref. 4,7,8). There are several questions that need to be addressed. The first is the relationship between the molar composition of the metal ions in the precipitated solids to that in solution, and the second question refers to the internal homogeneity of the so prepared particles. These
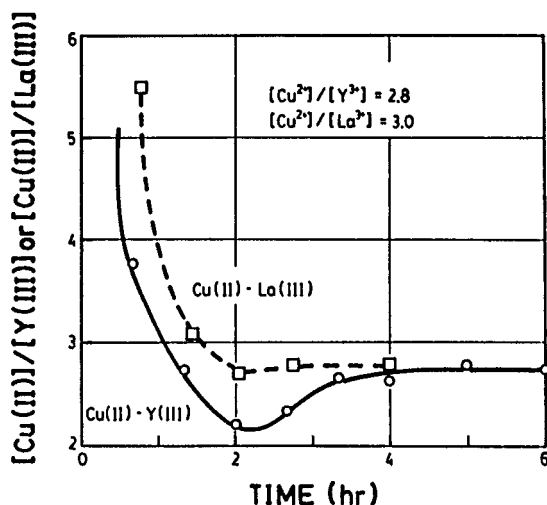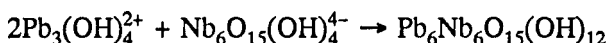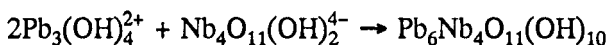
Fig. 4. The change of [Cu(II)]/[Y(III)] (solid) or [Cu(II)]/[La(III)] (solid) in particles as a function of time of aging at 90 °C of the following solutions: (———) 8.0×10^{-3} mol dm^{-3} in Y(NO$_3$)$_3$, 0.4 mol dm^{-3} in urea, and [Cu^{2+}]/[Y^{3+}] (soln) = 2.8; (———) 8.0×10^{-3} mol dm^{-3} in La(NO$_3$)$_3$, 0.5 mol dm^{-3} in urea, and [Cu^{2+}]/[La^{3+}] (soln) = 3.0 (ref. 7)

aspects of the precipitation from mixed solutions have been investigated on the systems [Cu(II)/ Y(III)] and [Cu(II)/La(III)] basic carbonates, which showed that the molar ratio in the particles changes with their growth (Fig. 4). After a sufficiently long time the molar ratio of the metals in the solids compares well to that in the original solutions. On calcination mixed metal oxides of definite stoichiometry are obtained (ref. 7). Again, it is necessary to continue such studies in order to relate the solubilities of the constituents to the kinetics of precipitation of solids of mixed composition.

Another kind of dispersions deal with particles of stoichiometrically defined metal oxides, such as various titanates, niobates, ferrites, etc. Again it was possible to obtain these complex materials by simultaneous decomposition of cationic and anionic complexes of two different metals at controlled rates. For example, spherical barium titanate particles were prepared by interaction of peroxidic complexes of Ba and Ti (ref. 9). By analogous procedures, lead titanate (ref. 10) and lead niobate (ref. 11) dispersions have been obtained, consisting of uniform particles of different shapes. A systematic review of relevant solution complexes indicated that the likely mechanisms for the formation of lead niobates are given by the equations.

$$2Pb_3(OH)_4^{2+} + Nb_4O_{11}(OH)_2^{4-} \rightarrow Pb_6Nb_4O_{11}(OH)_{10}$$

$$2Pb_3(OH)_4^{2+} + Nb_6O_{15}(OH)_4^{4-} \rightarrow Pb_6Nb_6O_{15}(OH)_{12}$$

COATED AND HOLLOW PARTICLES

In order to modify the surface characteristics of powders or to obtain materials of a given morphology, which cannot be achieved directly, it is advantageous to coat preformed particles with a layer of different chemical composition. Successful coatings have been produced with different starting inorganic powders covered with shells of other inorganic compounds (e.g., yttria on hematite or alumina on titania, etc.) (ref. 12–14). The thickness of the coated layers could be altered by the adjustments of the experimental conditions.
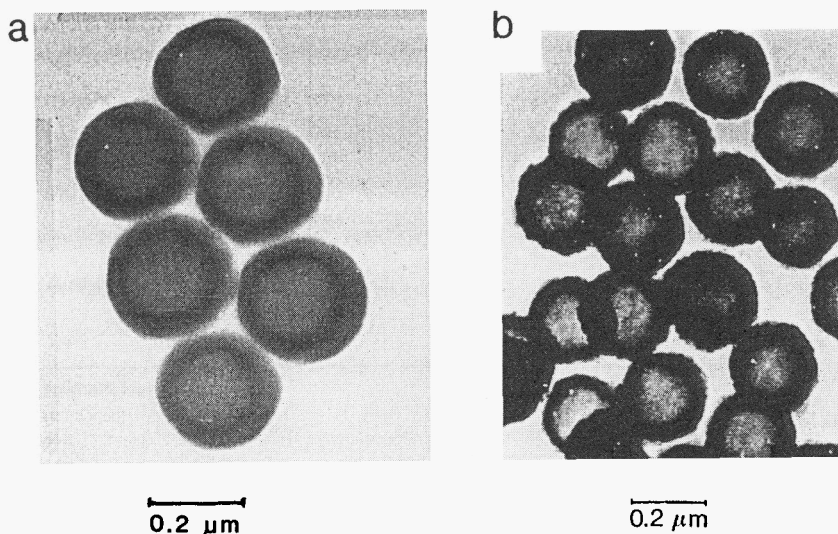
Fig. 5a. TEM of particles obtained by aging a dispersion containing 100 mg dm^{-3} poly-styrene (PS) latex 5 × 10^{-3} mol dm^{-3} Y(NO$_3$)$_3$, 1.1 mol dm^{-3} urea, and 1.2 wt% polyvinylpyrrolidone at 90 °C for 4 h; (b) hollow particles obtained by calcination of coated PS latex with yttria at 475 °C for 3 h (ref. 17)

More recently, shells of yttrium and zirconium compounds have been formed on polymer latexes (ref. 15,16). For example, TEM (Fig. 5a) shows a polystyrene latex coated with yttrium basic carbonate.

By careful calcination of particles illustrated in Fig. 5a at elevated temperatures in the presence of air, the polymer core can be vaporized, resulting in hollow yttria spheres of uniform size shown in Fig. 5b.

Acknowledgements

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