Preparation of monodispersed metal particles

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This review article deals with the preparation, characterization and mechanisms of formation of uniform simple and composite metal particles of different modal diameters and shapes. In principle, such dispersions can be obtained by reduction of metal ions, in uncomplexed or complexed state, with suitable reducing agents and appropriate additives. The effect of the redox potential in a given oxidation/reduction system on the nature of the final particles is discussed in some detail. In another approach monodispersed particles of metal compounds are prepared first and then reduced to pure metals either in a liquid or a gaseous medium. In doing so, one can produce powders of a given morphology by selecting the precursor particles of the desired shape. A special case is represented by coated particles, consisting of cores and shells of different chemical composition. Depending on the materials, it is possible to reduce either one or both components by appropriate chemical reactions.

Uniform colloids have fascinated scientists for a long time. Originally, the interests in such systems were mostly concentrated within the academic communities, which recognized that many properties of materials depended not only on their chemical composition, but also on particle size, shape and structure. Once monodispersed matter became available, it was possible to relate various characteristics (optical, magnetic, electric, adsorptive, catalytic, *etc.*) to the morphology and degree of dispersity of the final products.

More recently, the importance of well-defined particulates, ranging in modal size from several nanometers to several micrometers, has been recognized in numerous applications, including ceramics, pigments, catalysts, electronics, medical diagnostics and other areas, especially of high technology and medicine.

Several widely different techniques have been developed that can yield uniform powders. From the application point of view, the precipitation from homogeneous solutions is the most convenient, because it can yield the greatest variety of dispersions in terms of their particle characteristics by varying experimental parameters, which include the concentration of reactants, temperature, pH and the addition of seeds, stabilizers, oxidation/reduction agents, polymers, *etc.*[1–3] Furthermore, it is quite possible to produce by this method colloids of simple or mixed (internally or externally) chemical compositions.[4,5]

The uniform particles so obtained can then be altered, either in terms of their chemical composition or structure, by calcination of the powders, or by reduction or oxidation reactions by interactions in gases or solutions.

This review deals specifically with the preparation of uniform metal particles of nanometer to micrometer size. The interest in these materials has escalated, because they show superior performances as catalysts and in electronic, optical, medical and other applications. It is noteworthy that colloidal gold, described by Faraday more than a century ago,[6] is probably the first monodispersed system ever reported in the literature.

Recently, many methods to produce metal powders of various sizes and shapes have been reported (vapor phase reactions, aerosol thermolysis, plasma atomization, vapor deposition, *etc.*[†]), yet chemical precipitation from solutions is again probably the most versatile, economical and easy to perform procedure.[7] However, preparation techniques, especially of very small particles, involving the use of high concentrations of surfactants, such as precipitation in microemulsions, *etc.*, will not be included in the present review.

The 'solution route' to synthesize finely dispersed metal powders can be conducted in two distinct ways: (*i*) direct precipitation of particles from homogeneous solutions using appropriate reducing agents, and (*ii*) preparation of finely dispersed particles of metal compounds, followed by subsequent conversion to metals of essentially the same shape through reduction in solution or gas phase, at ambient or elevated temperature and pressure.

Preparation of Metal Particles in Homogeneous Solutions

Reduction mechanism

The reduction of oxidized metallic species leading to neutral atoms, the building blocks of metal particles, is the result of redox reactions in which electrons from a reducing agent are transferred to the metal according to the following schematic chemical equation:

$$m\mathrm{Me}^{n+} + n\mathrm{Red} \rightarrow m\mathrm{Me}^{0} + n\mathrm{Ox} \tag{1}$$

The driving force of the reaction is the difference between the redox potentials of the two half cell reactions, ΔE. The magnitude of ΔE determines the value of the equilibrium constant of the reaction, K_e, according to the well-known

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[†] Since these methods are not discussed here, the following review articles may be consulted for more detailed information: W. Romanowsky, *Highly Dispersed Metals*, Horwood (Wiley), Warsaw, 1987; ed. A. Furstner, *Active Metals. Preparation, Characterization, Applications*, VCH, Weinheim, 1996; P. Cintas, *Activated Metals in Organic Synthesis*, CRC Press, Boca Raton, FL, 1993; K. J. Klabunde, *Free Atoms, Clusters, and Nanoscale Particles*, Academic Press, San Diego, CA, 1994.

Table 1 Guidelines for the choice of reducing agents and reaction conditions in the precipitation of metal particles

Metal species	E^0/V	Reducing agent	Conditions	Rate
$Au^{3+,+}$, $Pt^{4+,2+}$, Pd^{2+}, Ag^+, Rh^{3+}, Hg^{2+}, Ir^{3+}	$\geqslant +0.7$	Organic acids, alcohols, polyols	$\geqslant 70$ °C	Slow
		Aldehydes, sugars	<50 °C	Moderate
		Hydrazine, H_2SO_3, H_3PO_2	Ambient	Fast
		$NaBH_4$, boranes, hydrated e^-	Ambient	Very fast
Cu^{2+}, Re^{3+}, Ru^{3+}	$< +0.7$ and $\geqslant 0$	Polyols	>120 °C	Slow
		Aldehydes, sugars	70–100 °C	Slow
		Hydrazine, hydrogen	<70 °C	Moderate
		$NaBH_4$[60]	Ambient	Fast
Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, In^{3+}, Sn^{2+}, Mo^{3+}, W^{6+}	<0 and $\geqslant -0.5$	Polyols	>180 °C	Slow
		Hydrazine, hydroxylamine	70–100 °C	Slow
		$NaBH_4$, boranes[14,60]	Ambient	Fast
		Hydrated e^-, radicals	Ambient	Very fast
Cr^{3+}, Mn^{2+}, Ta^{5+}, V^{2+}	< -0.6	$NaBH_4$, boranes[14]	T, $P >$ ambient	Slow
		Hydrated e^-, radicals	Ambient	Fast

relationship:

$$\ln K_e = nF\,\Delta E/RT \qquad (2)$$

where F, R and T have the usual meanings.

The reduction reaction is thermodynamically possible only if ΔE is positive, which implies that the redox potential of the reducing agent must have a more negative value than that of the metallic species. This difference should be larger than 0.3–0.4 V; otherwise, the reaction may not proceed or proceed too slowly to be of any practical importance. Thus, strongly electropositive metals like Au, Pt, Pd, Ag, Rh ($E_0 > 0.7$ V) will react even with mild reducing agents under ordinary conditions, while more electronegative metals ($E_0 < -0.2$ V) require very strong reducing agents and, frequently, extreme conditions of temperature and pressure. Table 1 gives a list of reagents most widely used in the precipitation of metals along with brief guidelines regarding the appropriate conditions.

When a metal reacts with reducing agents of significantly different strengths, it is possible to establish experimentally temperatures at which the process proceeds at a comparable rate leading to particles of the same size, yet of different internal structure, that is, degree of crystallinity. Fig. 1 illustrates two samples of uniform copper particles prepared with two reducing agents of different strength, at adjusted temperatures. Although similar in size, the powder produced with polyol at a higher temperature is more crystalline and less reactive towards oxygen than the sample reduced with hydrazine, making the former more suitable for certain practical applications.

The selection of an appropriate reducing agent and working conditions listed in Table 1 is applicable only for uncomplexed metal ions. If metallic species are involved in the formation of solute complexes or compounds, the standard redox potential, E_0, will be lower. The decrease in the potential depends on the stability of these complexes or compounds, as reflected in the value of the stability constant, K_β, or the solubility product, K_{sp}. For example, Table 2 presents the changes in the redox potential of the Ag^+ ion due to the formation of complexes with increasing stability. The consequence of this effect is a drastic limitation in the choice of reducing agents capable of reducing a metal and the need for harsher conditions as the stability of its complex increases. On the other hand, changing the value of ΔE through skillful manipulations of metal complex chemistry can be used to tailor the reactivity of the species in a given metal–reducing-agent system.

Table 2 Changes in the redox potential of Ag^+ ion as a result of complex formation

Redox system	$-\log K_\beta$	E_0/V
$Ag^+ + e^- \rightarrow Ag^0$	—	$+0.799$
$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag^0$	7.2	$+0.38$
$[Ag(SO_3)_2]^{3-} + e^- \rightarrow Ag^0 + 2\,SO_3{}^{2-}$	8.7	$+0.29$
$[Ag(S_2O_3)_2]^{3-} + e^- \rightarrow Ag^0 + 2\,S_2O_3{}^{2-}$	13.4	$+0.01$
$[AgI_4]^{3-} + e^- \rightarrow Ag^0 + 4\,I^-$	15.0	-0.09
$[Ag(CN)_3]^{2-} + e^- \rightarrow Ag^0 + 3\,CN^-$	22.2	-0.51

The formation of different complexes is not the only tool available to alter the reactivity of a metal through ΔE manipulations. The majority of redox systems in aqueous solutions involve H^+ and OH^- ions. As a result, the pH of the reaction medium can have a major impact upon the redox potential of the solutes, as predicted by the Nernst equation. Since metal

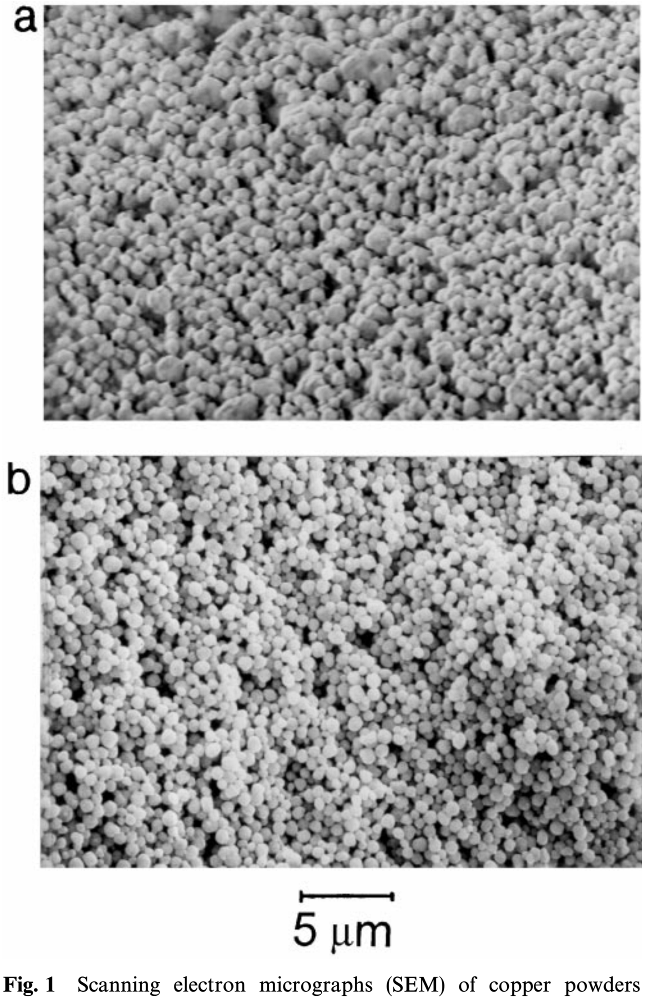

Fig. 1 Scanning electron micrographs (SEM) of copper powders reduced with (*a*) propylene glycol at 150–160 °C and (*b*) hydrazine at 60–70 °C

species and reducing agents can be affected simultaneously by the pH, the overall effect upon ΔE and, consequently, the reduction process may be rather involved.

The two parameters described above, complexation and the pH, are rarely separated in practice. The overall effect can be condensed into the so-called 'redox diagrams', which provide useful information on how to manipulate the reaction to generate metal particles of the desired structure and size. These schemes may be constructed for more than one metal, in order to control their relative reactivities in the preparation of composite particles. As an example, Fig. 2 displays the diagram for Pd^{2+}, Ag^+ and hydrazine when the pH of the solution is adjusted with ammonia, which also strongly complexes both metal ions.

As predicted by eqn. (2), an increase in the value of ΔE will translate into a more spontaneous reaction, leading to smaller sized metal particles due to the generation of a larger number of nuclei. This effect is illustrated in Fig. 3, which displays scanning electron micrographs of four palladium samples prepared by reduction with hydrazine of Pd^{2+} complexed with different amounts of ammonia, under otherwise the same experimental conditions; the size of the final metal particles decreases as ΔE of the reaction increases. Following this rationale, reduction reactions with very large ΔE must be employed to generate nanosized metal particles, which implies the selection of uncomplexed metal ions coupled with very strong reducing agents. However, the requirement of a large ΔE is a necessary, but not sufficient condition to achieve such monodispersed small particles. Other aspects of the system, which may affect the aggregation (ionic strength, particle charge and the presence of surfactants) play an important role in determining the properties of the final dispersion.

In some instances ligand molecules can act simultaneously as reducing agents. For example, stable nickel and cobalt dispersions were obtained by aging the respective salt solutions in the presence of triethanolamine in basic solutions at elevated temperatures. Depending on conditions, particles of different shapes and of large sizes (up to 20 μm) could be produced by this procedure.[8] Fig. 4 illustrates two samples prepared as described in the legend.

Solvent effect

The reduction of oxidized metallic species in solution can be performed in both aqueous and non-aqueous media. Since many metal compounds are soluble in water, the preparation of metal particles in aqueous solutions is relatively easy to perform and the mechanisms of the reactions have been well-studied.[6,9–13] In contrast, synthesis in non-aqueous solvents presents serious difficulties. The first major obstacle is the low solubility and dissociation of most metallic compounds and ionic reducing agents in low polarity liquids, making the transfer of electrons in solution difficult, if not impossible. Consequently, the precipitation in non-polar solvents is limited to organometallic compounds and suitable reducing agents, which are soluble in the specific medium. By using organoborates, for example, nanosized particles of a number of metals have been obtained by reduction in tetrahydrofuran.[14]

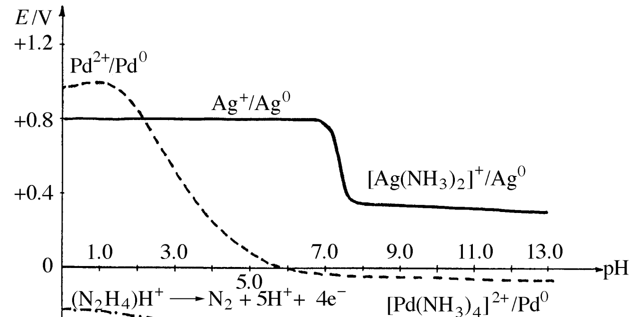

Fig. 2 The effect of pH on the redox potential of hydrazine and of ammonia–metal complex formation on the redox potential of palladium and silver ions

With increasing polarity of the organic solvent, the solubility and the dissociation of the metallic compounds also increase and the list of possible reduction reactions grows accordingly. Thus, the synthesis of metal particles in alcohols has been routinely carried out.[15–19]

Another major issue involving organic solvents of lower polarity is a weaker electrostatic stabilization associated with the low dielectric constant, leading to particle aggregation. For these reasons, the availability of effective dispersing agents (*e.g.*, surfactants) is usually necessary to obtain a stable dispersion of metal particles in such media.

An interesting case is represented by solvents that can play a multiple role in the chemical preparation of metal particles. Primary alcohols (methanol, ethanol) may function both as solvents and reducing agents in the preparation of Pd, Pt and Au particles, while polyols (glycerol, diethylene glycol) can play a triple role (as solvents, reducing agents and stabilizers) in the preparation of Cu and Ni particles.[20]

Mechanism of particle formation

Metal atoms generated by reduction in homogeneous solutions are essentially insoluble in the liquid and, therefore, gradually aggregate into clusters, called embryos:

$$x\mathrm{Me}^0 \rightleftarrows (\mathrm{Me}^0_x)_{\mathrm{em}} \qquad (3)$$

The embryos are dynamic entities involved in a continuous dissociation-condensation process and as such they still represent a true solution phase. It is interesting to note that very small metal clusters, those containing a number of atoms corresponding to the so called 'magic numbers', are more stable. The embryos of intermediate sizes probably either dissociate or grow to reach these favored states.[21]

As new metal atoms are generated in a system, embryos reach a critical size and separate from the solution as solid particles, the nuclei $(\mathrm{Me}^0_n)_{\mathrm{nucl}}$:

$$(\mathrm{Me}^0_x)_{\mathrm{em}} + y\mathrm{Me}^0 \rightarrow (\mathrm{Me}^0_{x+y})_{\mathrm{nucl}} \qquad (4)$$

The number and the size of the nuclei depend on many parameters in the precipitation reaction, such as the solute concentration, redox potential of the reduction reaction, temperature, the nature and the concentration of the surfactant, solvent viscosity and surface tension.

Nucleation is seldom the final stage in the formation of metal particles unless special precautions are taken. By further addition of metal atoms, the nuclei grow to primary (nanosize) particles:

$$(\mathrm{Me}^0_n)_{\mathrm{nucl}} + m\mathrm{Me}^0 \rightarrow (\mathrm{Me}^0_{n+m})_{\mathrm{pp}} \qquad (5)$$

These primary particles are, as a rule, unstable because they represent a system of large free energy. The diffusion of atoms onto them may continue [eqn. (6)] or they can aggregate [eqn. (7)] to form the final metal particles $(\mathrm{Me}^0)_{\mathrm{p}}$:

$$(\mathrm{Me}^0)_{\mathrm{pp}} + n\mathrm{Me}^0 \rightarrow (\mathrm{Me}^0)_{\mathrm{p}} \qquad (6)$$

$$m(\mathrm{Me}^0)_{\mathrm{pp}} \rightarrow (\mathrm{Me}^0)_{\mathrm{p}} \qquad (7)$$

While the diffusion mechanism [eqn. (6)] translates into a slow growth of primary particles, usually to submicrometer size, the aggregation mechanism [eqn. (7)] can lead to a faster

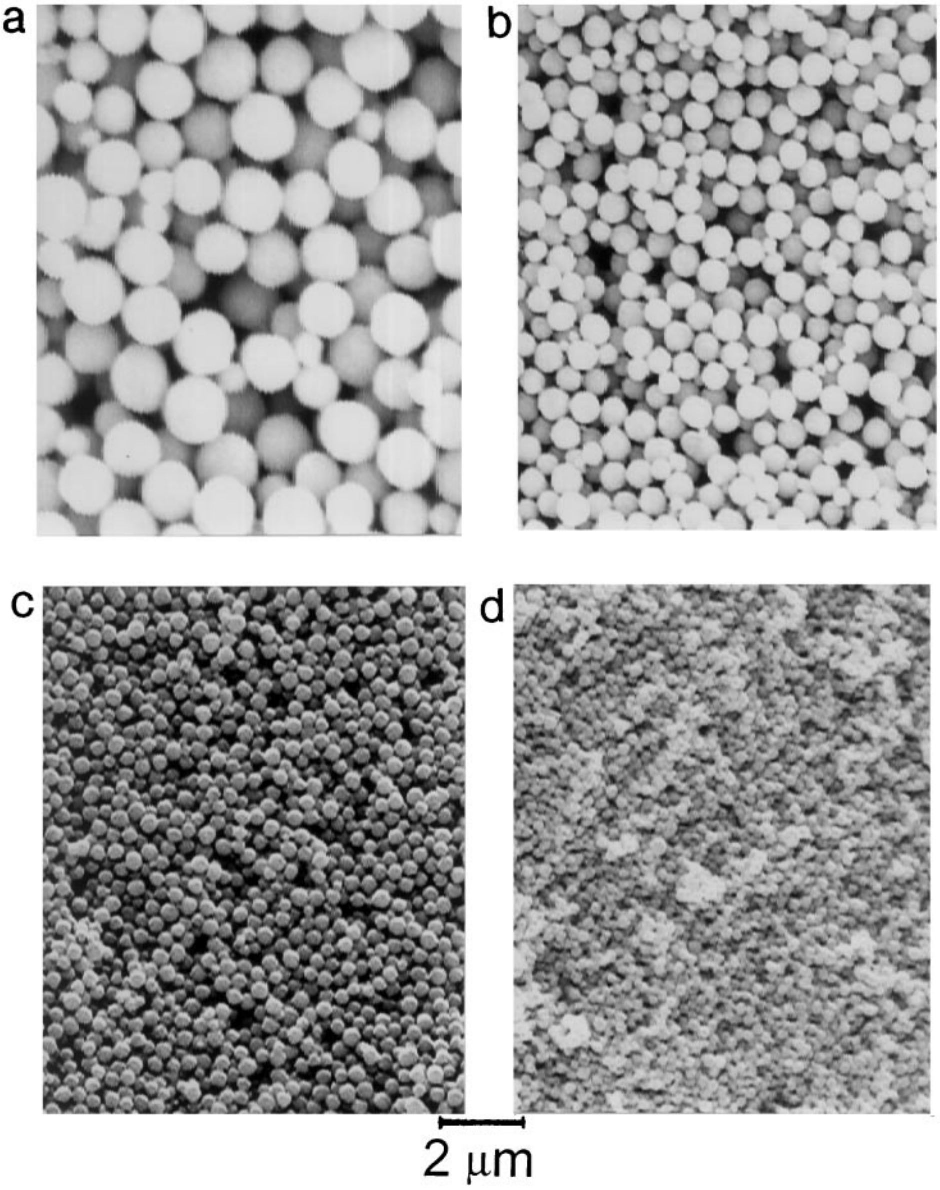

Fig. 3 SEM of Pd powders prepared by reducing $Pd(NO_3)_2$ solutions containing different amounts of ammonia, with hydrazine, at 20 °C and pH: (*a*) 3.0, (*b*) 2.0, (*c*) 1.4 and (*d*) 0.8

increase into larger particles (up to several micrometers), depending on the number of primary particles (m) involved in the process.

Intuitively, one would expect *monodispersed* colloids to form by diffusional growth as suggested by LaMer and Dinegar.[22] However, recently it has been demonstrated, on a large number of examples involving the preparation of well-defined dispersions, that this mechanism is applicable mostly when final products consist of amorphous particles. Instead, nanosized precursors, once produced, aggregate to larger yet uniform particulates, which can be either spherical or of other shapes.[1,23–25] This mechanism is essentially observed if the resulting solids show X-ray patterns indicating crystallinity, although particles do not consist of single crystals.

In order to produce stable dispersions of nanosized metal powders the aggregation process must be arrested in the early stages of particle formation. This objective can be achieved by electrostatic, steric, electrosteric and hydration mechanisms of stabilization. The electrostatic stabilization, based strictly on manipulating the balance between attractive and repulsive forces, has little impact in concentrated systems, where the double layer is compressed due to the high ionic strength. For dilute systems, however, the impact of charge can be quite effective and it has the advantage of leading to stable dispersions of metals with very clean surfaces, a key condition for success in catalysis. The hydration stabilization mechanism is quite a potent tool in the case of nanosized, hydrophilic solids, but is less effective in the stabilization of metal particles. Steric and electrosteric stabilization, consisting in adsorption of surfactant, polymer or polyelectrolyte molecules on metal particles, cause a screening of the unbalanced attractive van der Waals forces. Both approaches are especially useful in the case of concentrated dispersions of larger metal particles.

The effectiveness of various stabilizers (or dispersants) depends greatly on the system of interest. Although attempts were made to quantify the stabilizing capability of various polymers or surfactants and eventually to predict their performance,[26] the selection of a good dispersant for a specific it is possible to identify dispersants that are not only effective but can simultaneously perform the role of a reducing agent as well.[27,28]

Particle shape, structure and size

As it was shown above, at any time during the consolidation of metallic particles in solution, two possibilities for growth are available: (*i*) *via* attachment of elemental building blocks

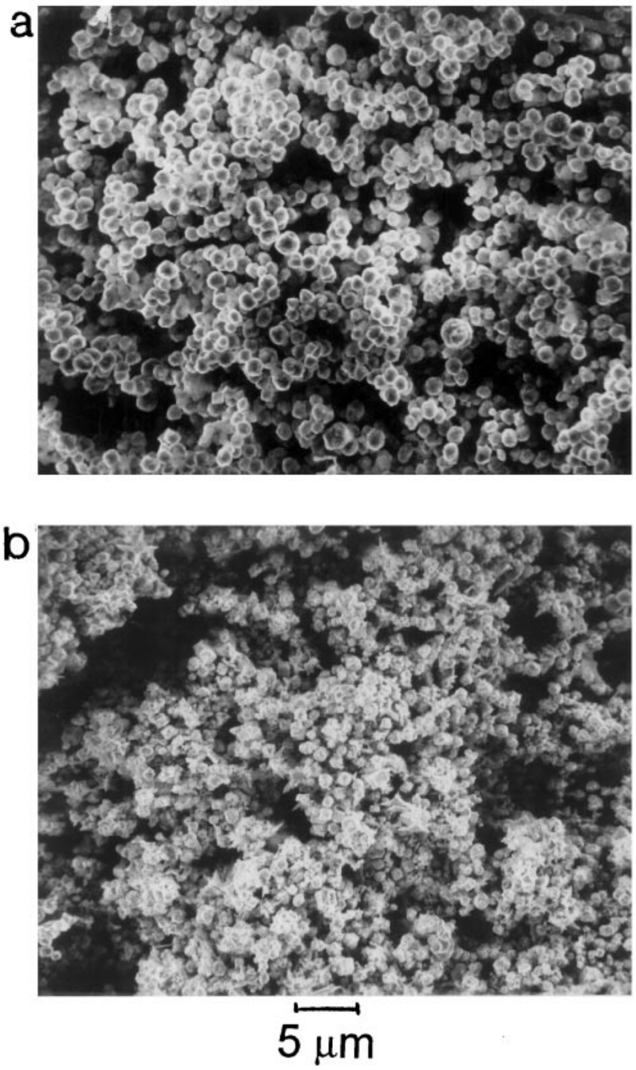

Fig. 4 SEM of (*a*) nickel particles precipitated in solutions initially containing 0.04 mol dm^{-3} $NiCl_2$, 0.2 mol dm^{-3} triethanolamine (TEA) and 1.2 mol dm^{-3} NaOH upon hydrothermal aging at 250 °C for 1 h and (*b*) cobalt particles obtained under the same conditions except $Co(ClO_4)_2$ was used as the starting electrolyte

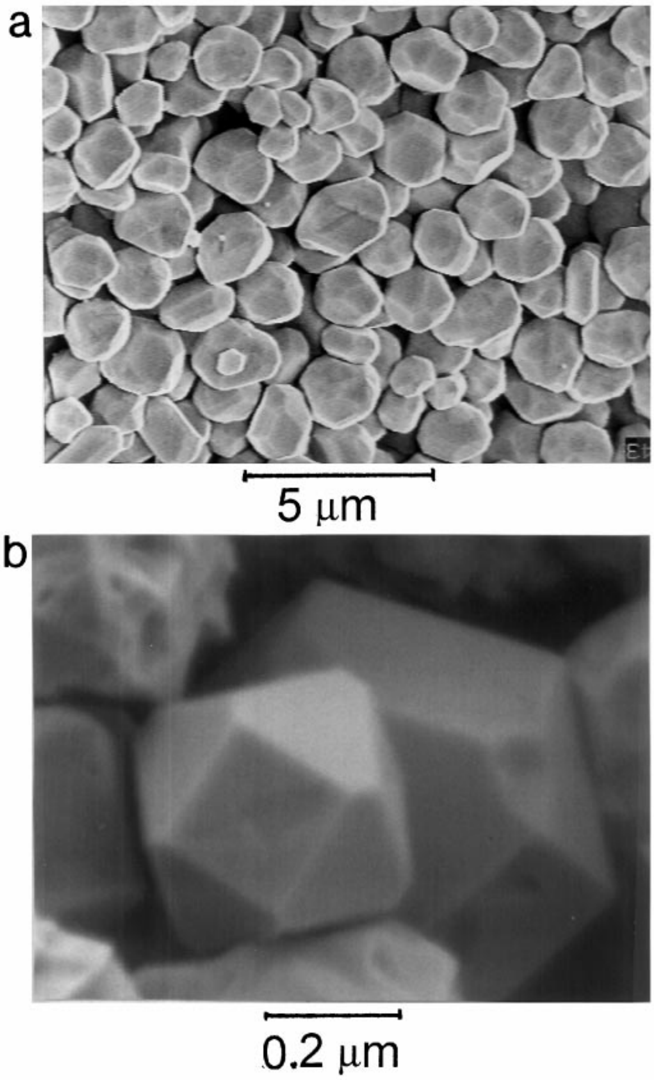

Fig. 5 SEM of (*a*) crystalline gold particles produced by reducing $HAuCl_4$ with glycerol at 130 °C and (*b*) palladium crystalline particles prepared by reduction of $PdCl_2$ with ascorbic acid at 25 °C

(neutral metal atoms) onto already formed particles and (*ii*) through aggregation or attachment of already formed particles. These two distinct routes help in explaining many findings related to the structure, shape and size of the finely dispersed metals.

It is to be expected that the growth mechanism involving only incorporation of additional metal atoms onto nuclei will favor the development of crystals of metal of regular shape (facets, edges) with few irregularities in their lattice, dense, and with very little internal grain boundary. Fig. 5 illustrates crystalline Au and Pd formed by this mechanism. In contrast, metal particles formed through an aggregation mechanism will be mostly spherical and polycrystalline, having large internal grain boundaries and, consequently, a lower density as illustrated in the example of gold powder in Fig. 6.

In reality it is likely that mechanisms involving both growth and aggregation frequently take place in the same system. Depending on the prevailing process, the polycrystallinity, internal grain boundary, density and shape of the final particles will be between the extreme cases presented above. For example, Fig. 7 displays a gold dispersion in which the nuclei have grown to larger subunits, which then underwent aggregation into larger particles.

The final size depends on the supersaturation, the fraction of solute species involved in the nucleation step, relative to the total amount of metal in the system, and on the extent of aggregation. High supersaturation of metal atoms will generate a large number of nuclei consuming a major fraction of the metal species in the system. If the aggregation mechanism is inhibited, subsequent increase in size will reflect only growth by exhaustion of the remaining metallic species in solution and the final particles will remain in the nanosize range. Consequently, reduction of uncomplexed metallic species with strong reducing agents in efficiently stabilized systems is recommended, if stable nanosized dispersions are desired.

To produce larger particles (in the submicrometer and micrometer range) by diffusional growth, a small number of nuclei should be generated, using up only a minor fraction of the available metal species, which subsequently grow at the expense of the remaining metal in solution. This condition can be realized by slow reactions, added seeds, or slow and gradual addition of metallic species into the system. Inherent in this mechanism is the condition that the existing particles are stable, that is, aggregation is prevented.

The final size of metal particles produced by aggregation depends on the ionic strength of the dispersion, surface charge of the primary particles and the nature of additives. By the adjustment of these parameters, it is possible to produce monodispersed colloidal metals over a wide range of modal sizes.

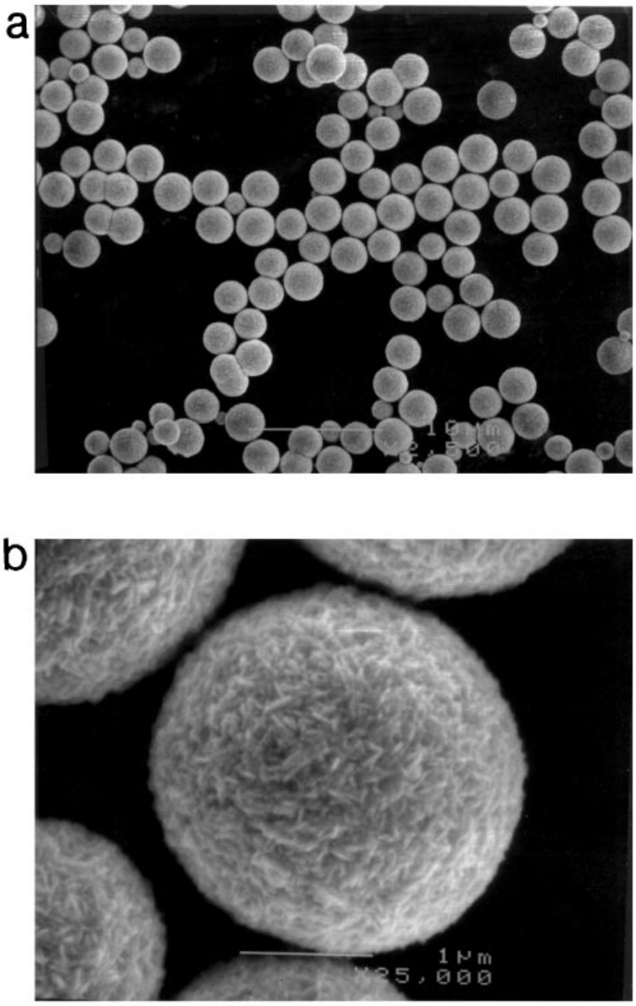

Fig. 6 (*a*) SEM of gold particles obtained by rapid addition of $HAuCl_4$ in an aqueous solution of ascorbic acid at 20 °C. (*b*) The same particles at a higher magnification

Composite metal particles

In principle, precipitation in a homogeneous solution containing two or more metal salts can be used to prepare composite dispersed solids. Depending on the conditions, the resulting particles may be internally inhomogeneous, that is, their composition changes from the core to the periphery.[29–31] However, if the process is conducted sufficiently fast, a homogeneous mixed solid phase can be achieved.[32] The same effects are observed with composite colloidal metals.[33,34] During the reduction, the metal species having the highest redox potential will precipitate first, forming the core of the particle, followed by the coprecipitation of the second component, which prevails at the surface.[35–37] The sequence of precipitated species can be reversed by complexation with a ligand that forms a significantly stronger complex with the core-forming metal. Fig. 8 shows spherical particles of Ag/Pd (wt ratio 70 : 30%), consisting of a silver 'core' and a palladium 'shell', obtained by precipitation in ammoniacal solution containing the two metal salts and hydrazine. Although palladium is more electropositive than silver, complexation with ammonia reverses the order of the reaction, as shown in the redox diagram in Fig. 2.

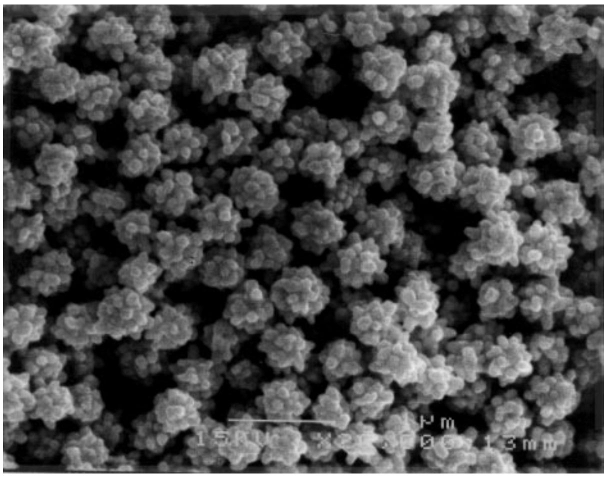

Fig. 7 SEM of gold particles prepared by mixing aqueous solutions of $HAuCl_4$ (0.5 mol dm^{-3}) and ascorbic acid (0.75 mol dm^{-3}) at 20 °C, using the 'controlled double jet precipitation' (CDJP) process

When the redox potentials of the two metals are similar ($E_0^1 \cong E_0^2$) and ΔE of the reduction reaction is large, true bimetallic alloy particles can be obtained.[38,39] If the redox potentials of the two metals are significantly different, the manipulation of metal chemistry and the utilization of special precipitation techniques, such as the 'controlled double jet precipitation' (CDJP) process, are necessary to ensure formation of composite alloy particles. Fig. 9 shows a Ag/Pd alloy powder (wt ratio 70 : 30%) prepared by reducing a mixture of metal nitrates with ascorbic acid in acidic solution at ambient temperature.

Phase Transformation

As discussed above, precipitation of fine colloidal metals directly from solutions is possible only in a limited number of cases, which are essentially determined by the availability of a suitable reducing agent for the cation in question. It is also important to note that the described procedures yield mostly spherical particles.

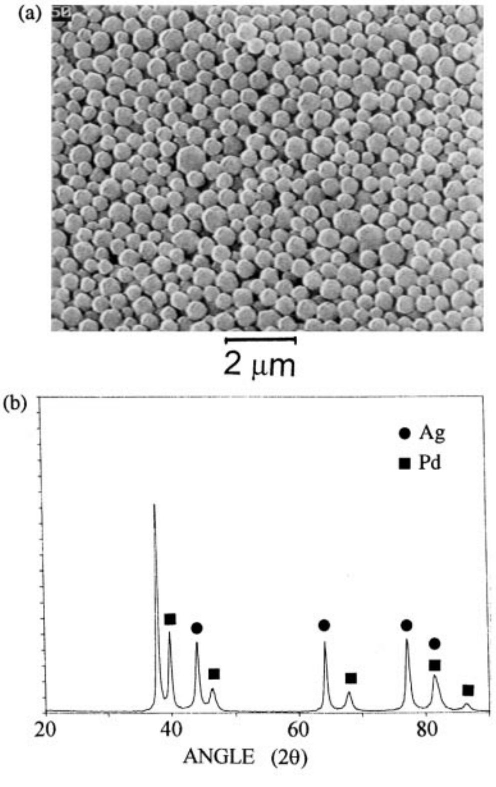

Fig. 8 (*a*) SEM of Ag/Pd particles (wt ratio 70 : 30%), obtained by reducing with hydrazine, at 25 °C and pH 9.5, a solution containing silver and palladium ammonia complexes. (*b*) XRD of Ag/Pd particles synthesized as in (*a*) showing two distinct metal phases

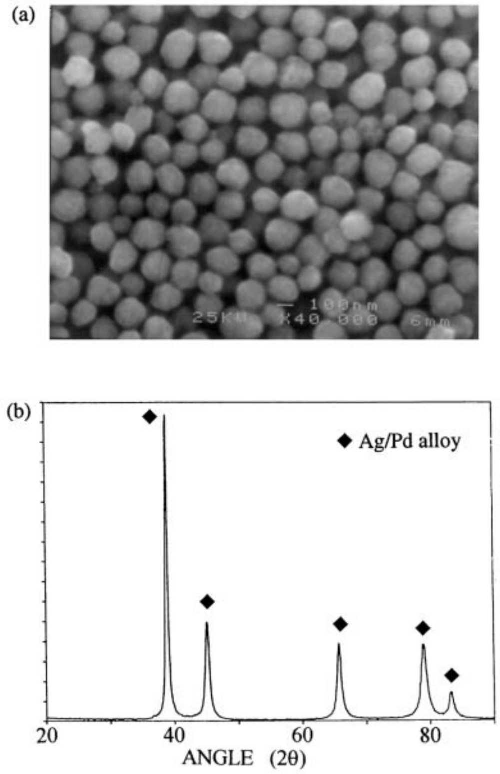

Fig. 9 (*a*) SEM of Ag/Pd alloy particles (wt ratio 70 : 30%) prepared by reducing a solution of mixed metal nitrates with ascorbic acid at 20 °C. (*b*) XRD pattern of the same Ag/Pd alloy particles showing the presence of a homogeneously mixed crystal lattice

Another avenue of approach to produce monodispersed metal colloids is first to synthesize different compounds, mostly metal (hydrous) oxides, and then reduce such particles either in liquid dispersions or as solid powders. In the latter case hydrogen at elevated temperatures can be commonly used. In addition to broadening the opportunities to prepare uniform metal powders, the phase transformation process makes it possible to obtain particles of different shapes, by choosing precursors of a given morphology and preserving it during the reduction procedure. Several examples of the resulting products by the described procedure are offered below.

Reduction in liquid dispersions

Palladium. Uniform spheres of Pd ranging in modal diameters between 0.1 and 7 μm were obtained by first reacting aqueous $PdCl_2$ solutions with urea at elevated temperatures (75–90 °C) in the presence of a nonionic surfactant (Triton X-405), and subsequently reducing the resulting particles with hydrazine.[40] The original solids consisted of a Pd–urea adduct, the composition of which varied with the experimental conditions. However, all these products were reduced with hydrazine to pure palladium spheres. In order to prevent aggregation of the precursors during the subsequent processing, polyvinylpyrrolidone (PVP) was added to the dispersions. Fig. 10(*a*), (*b*) illustrate the so-prepared spheres of original Pd–urea particles and the final Pd powder. During the transformation process the diameter was somewhat reduced and the particle surfaces became rougher.

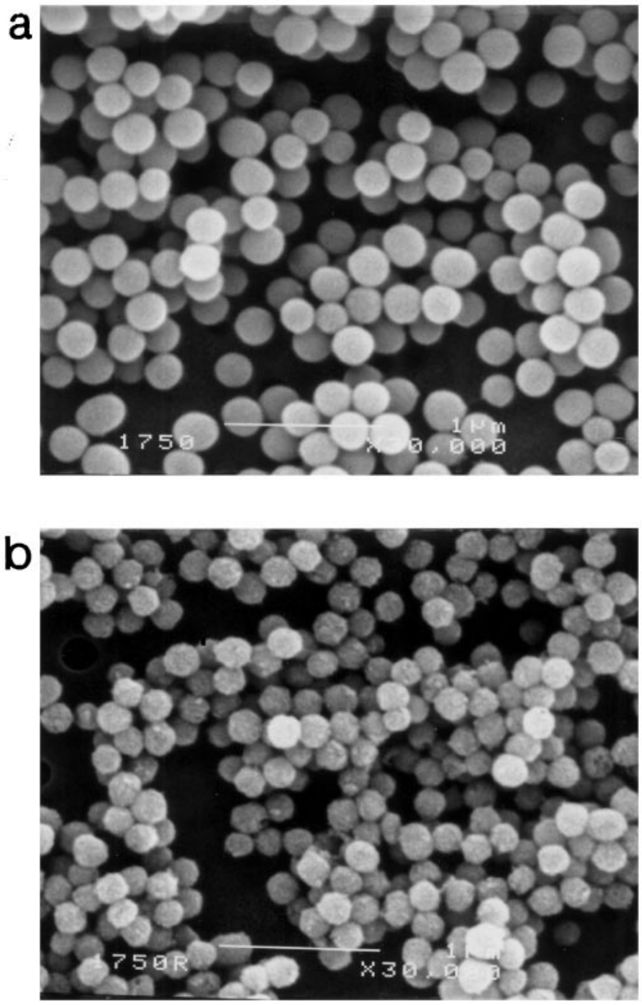

Fig. 10 (*a*) SEM of particles obtained by aging at 90 °C for 45 min a solution containing 4.0×10^{-3} mol dm^{-3} $PdCl_2$, 4.0×10^{-4} mol dm^{-3} urea, and 4×10^{-3}% Triton X-405. (*b*) Pd particles obtained by hydrazine reduction of the precursor particles illustrated in (*a*)

Copper. A number of uniform dispersions of copper compounds have been synthesized by precipitation from homogeneous solution.[41–43] Depending on the chemical processes involved, particles of various shapes (spheres, cubes, octahedra, *etc.*) and compositions could be obtained. For example, when solutions containing $Cu(NO_3)_2$ and urea were heated at 90 °C and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) was slowly added dropwise, spheres of copper basic carbonate were formed first, which then dissolved and cubic particles of metallic copper were finally obtained (Fig. 11). The reaction time varied between 30 min and 1 h, depending on the reactant concentrations, and so did the size of the resulting cubes over the range of 1 to 10 μm.[42]

Reduction of powders

A more direct phase transformation process involves the preparation of dispersions of uniform particles of metal compounds, separating them from the mother liquor and, after drying, contacting the powders with hydrogen gas at elevated temperatures. Since metal oxides are most commonly used in such reduction processes, it is sometimes necessary to convert the original powder of different chemical compositions (such as metal carbonates) into the oxide and then treat the product with hydrogen. The reduction process may itself proceed in stages, such as when the oxidation state of the metal changes from a higher to a lower value and finally to zero.

Copper. Hamada *et al.*[41] prepared spherical particles of copper(I) oxide of different diameters by reducing Fehling solutions with glucose,[43] and then further reduced these particles with hydrogen to pure copper at rather low temperatures (varying between 69 and 111 °C). The resulting spheres retained the original morphology but decreased in size as illustrated in Fig. 12. The reduction rate depended on the size of the precursors and a minimum temperature was needed

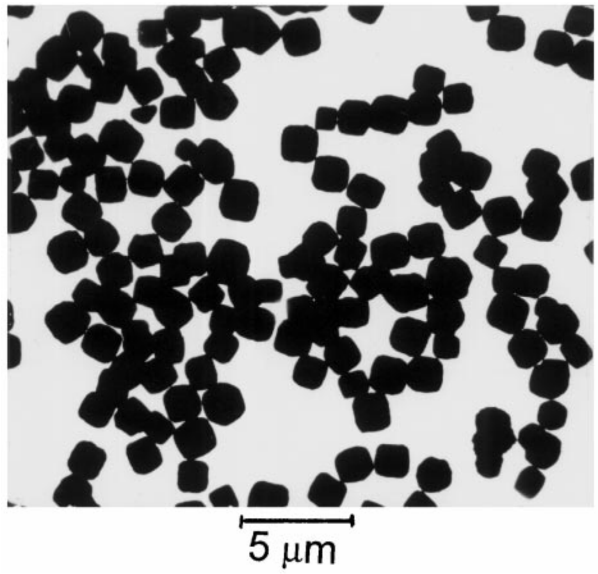

Fig. 11 Transmission electron micrograph (TEM) of cubic copper particles obtained by aging at 90 °C a solution containing 8.0×10^{-3} mol dm^{-3} $Cu(NO_3)_2$, 0.2 mol dm^{-3} urea and 1.0×10^{-3} mol dm^{-3} $NH_2OH \cdot HCl$.[42] (Reproduced by permission of Elsevier Science)

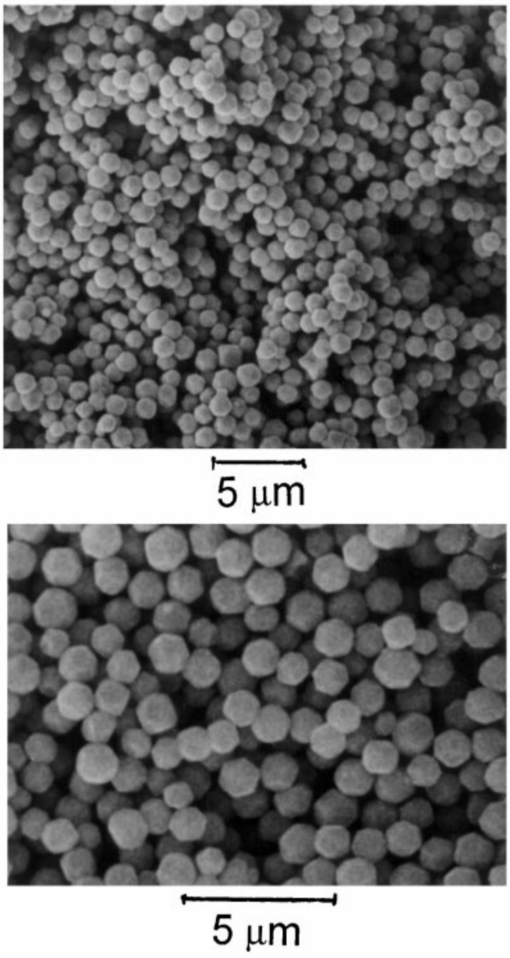

Fig. 12 (top) SEM of copper(I) oxide particles obtained by aging at 95 °C for 4 h 1000 cm^3 of a solution containing 1×10^{-2} mol dm^{-3} $CuSO_4$, 3×10^{-2} mol dm^{-3} potassium sodium tartrate, 6×10^{-2} mol dm^{-3} NaOH and 6.5×10^{-2} mol dm^{-3} glucose in a sealed glass bottle. (bottom) Copper particles obtained by reduction of the powder shown above with hydrogen at 91 °C

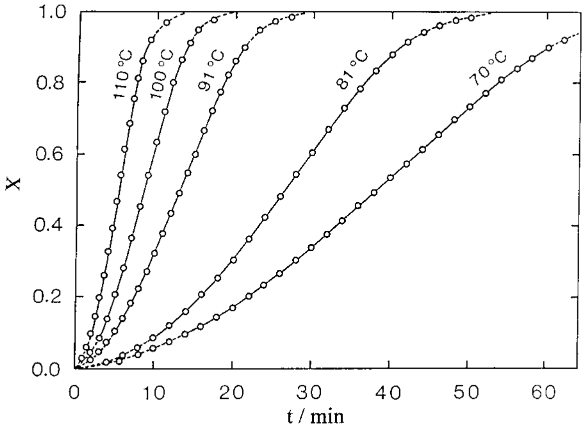

Fig. 13 Weight fraction of Cu_2O particles (0.46 µm in size) as a function of time, reduced at different temperatures under a hydrogen partial pressure of 101 kPa and a flow rate of 400 cm^3 min^{-1}

to bring the reaction to completion, as illustrated in Fig. 13. The shape of these curves indicates the autocatalytic nature of the reduction process.[41]

In another study, it was shown that spherical particles of copper(II) basic carbonate could be converted to pure copper either directly or by first dehydrating the starting powder to copper(II) oxide[42] by passing a stream of hydrogen heated to 140–200 °C over the powder for 1–2 h. As one would expect, longer times were needed for the transformation to Cu of copper(II) basic carbonate than of copper(II) oxide.

Iron. Uniform iron oxide particles, especially of hematite, have been prepared in a variety of shapes, including spheres, cubes, ellipsoids, needles, rods, *etc.*[44–46] It was shown that powders consisting of these dispersed solids can be reduced with hydrogen while preserving their morphology. The described approach makes it possible to produce finely dispersed iron of desired shapes. For example, monodispersed acicular particles with a length ranging between 0.1 and 0.5 µm are considered to be most desirable for recording tapes, because of their magnetic and stability properties.[47]

Powders of ellipsoidal hematite (α-Fe_2O_3) could be reduced in the presence of hydrogen at elevated temperatures, which determined the nature of the final products.[48] Thus, X-ray diffraction showed that samples heated at 350 °C consisted of

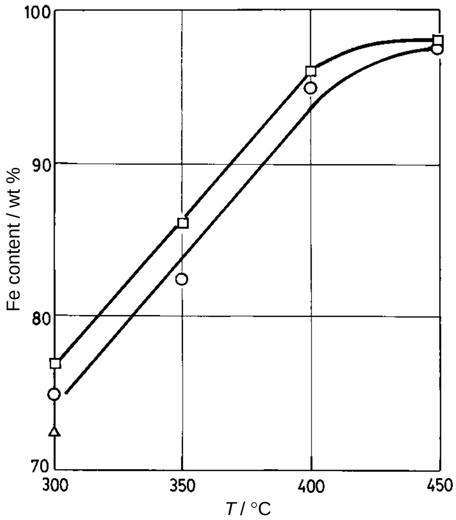

Fig. 14 Fe content (wt%) in products obtained from α-Fe_2O_3 powders by reduction with hydrogen at different temperatures using two ellipsoidal hematite precursor particles (○, □). The triangle gives the calculated percentage of iron in pure magnetite.[48] (Reproduced by permission of the American Chemical Society)

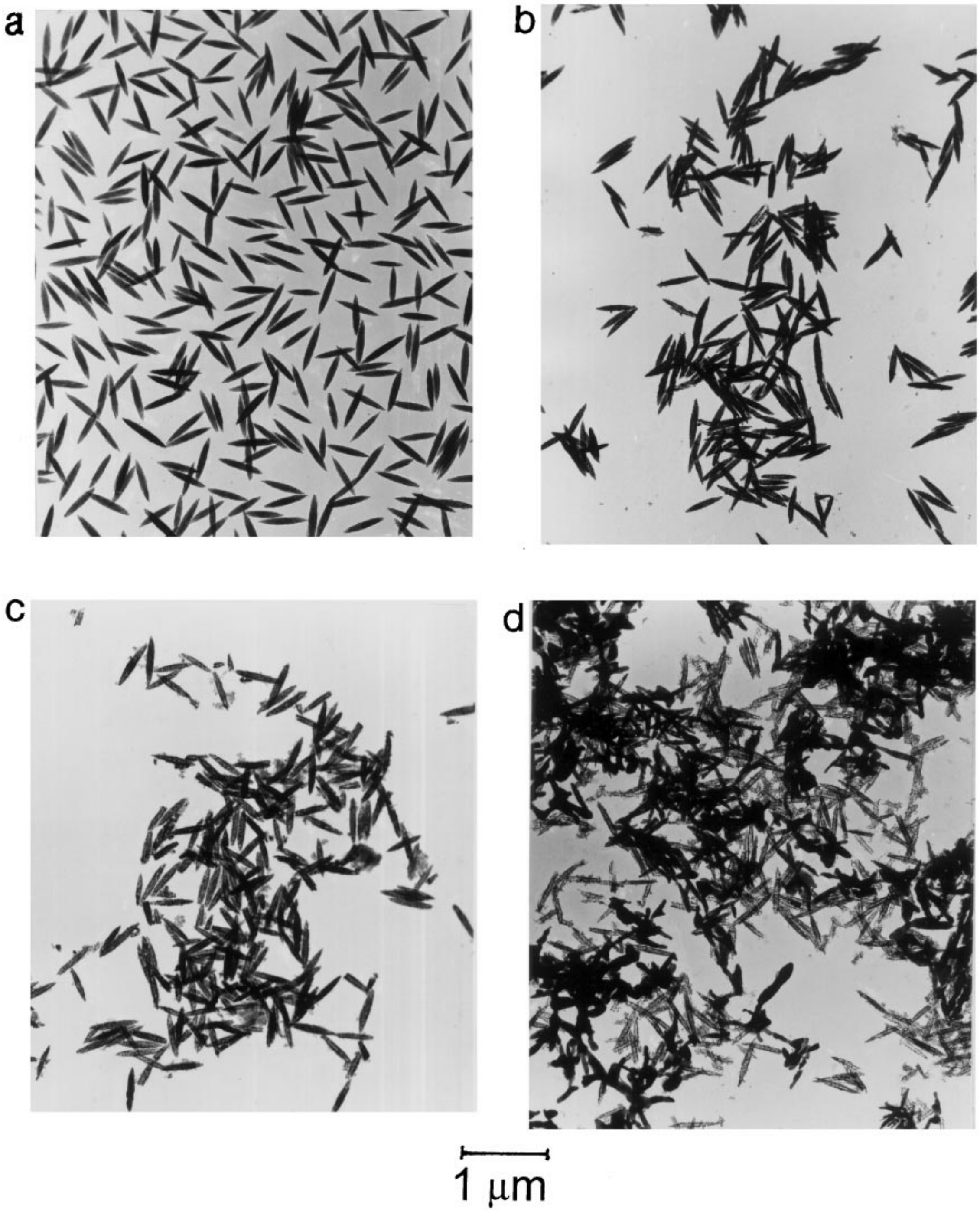

Fig. 15 (*a*) TEM of hematite (α-Fe_2O_3) powder and of particles obtained by reduction with hydrogen at (*b*) 350 °C, (*c*) 400 °C and (*d*) 450 °C.[48] (Reproduced by permission of the American Chemical Society)

magnetite (Fe_3O_4), those heated at 350 °C were a mixture of Fe_3O_4 and α-Fe, while at 400 °C essentially only α-iron was detected (Fig. 14). The transmission electron micrographs in Fig. 15 illustrate precursor hematite and the reduction products treated as described in the legend. The mean particle length remained essentially unchanged but the average size of internal crystallites became smaller in magnetite and larger in iron, as the temperature of the treatment in hydrogen increased (Fig. 16).

By a similar procedure, it was possible to reduce cubic hematite particles[49] into pure iron[50] at temperatures ranging between 250 and 380 °C, while preserving their shape. The reaction proceeded through two steps, the first yielding quantitatively magnetite, while the second resulted in iron. The latter stage followed an autocatalytic rate of transformation.[50]

Reduction of coated particles

Coating colloidal particles with a layer of a different composition may serve different purposes. For example, the shell may protect the core from chemical changes due to interactions with a liquid or gaseous environment in which the solids are dispersed. In some other instances, certain powders are not available in desired particle morphologies, but solids of a different composition can be produced in shapes as needed. It is then possible to use the latter as core materials onto which is deposited the original compound, thus achieving both the intended shape and the surface chemical composition. The coatings may be also used to alter the sign and the magnitude of surface charges, as well as magnetic, optical, adsorptive, catalytic and many other properties of dispersed matter.

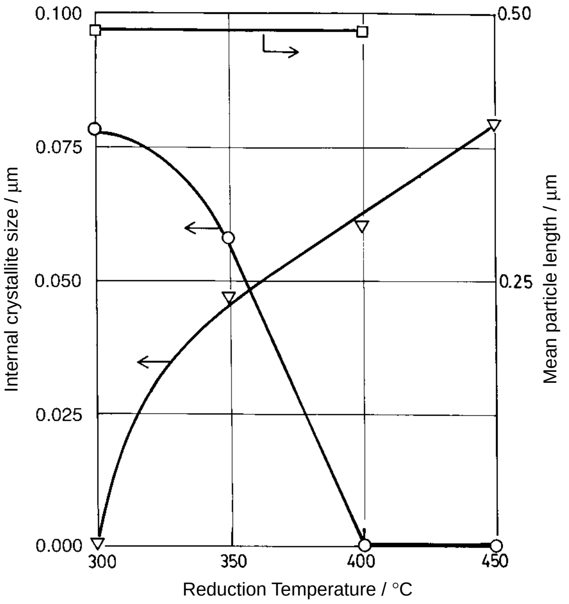

Fig. 16 Mean particle length (□) and internal crystallite size of magnetite (Fe_3O_4, 311) (○) and of iron (α-Fe, 110) (▽) obtained by reduction with hydrogen of a hematite powder as a function of the reduction temperature.[48] (Reproduced by permission of the American Chemical Society)

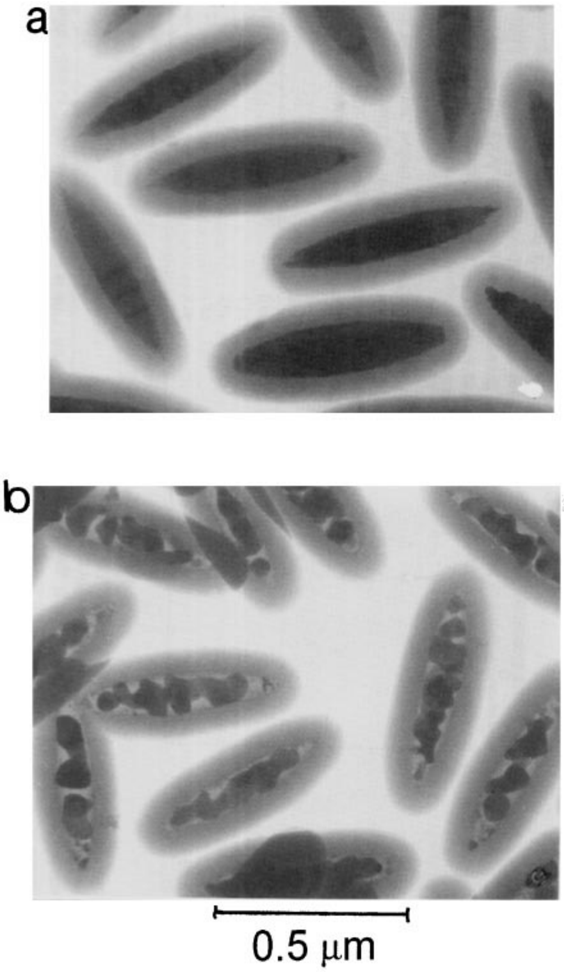

Fig. 17 TEM of hematite (α-Fe_2O_3) particles (*a*) coated with silica and (*b*) after reduction with hydrogen at 450 °C for 3 h.[56] (Reproduced by permission of Academic Press)

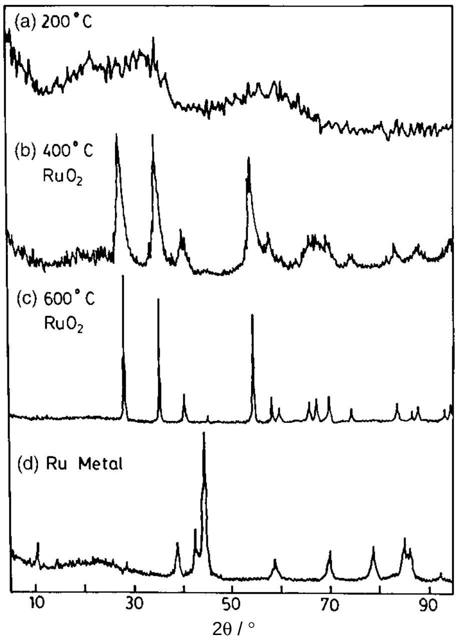

Fig. 18 X-Ray diffraction patterns of spherical amorphous composite ruthenium particles calcined at (*a*) 200 °C, (*b*) 400 °C and (*c*) 600 °C. (*d*) XRD of Ru metal obtained by reduction of the same powder with hydrogen at 250 °C.[55] (Reproduced by permission of Elsevier Science)

It has been amply demonstrated that uniform particles can be covered with layers of different thicknesses by precipitating the shell material onto the cores suspended in the reacting solutions.[4,5] Indeed, it is quite possible to produce inorganic coatings on inorganic or organic cores, and organic shells on inorganic particles. This chapter discusses the use of coated particles as precursors, with subsequent transformation of the core or the shell to metal. Several cases will be considered, including (*i*) reduction to metal of a core protected with an inert shell and (*ii*) simultaneous complete or partial reduction of both the core and the shell. In principle, there is no reason why a shell of a metal oxide on an inert core could not be reduced to pure metal.

Reduction of cores. It has been shown that silica coatings on inorganic cores of different metal oxides can be quite readily achieved by the hydrolysis of tetraethyl orthosilicate (TEOS) or of sodium silicate in the presence of preformed particles, such as hematite[48,51] or yttria.[52] Alternatively, nanonsized

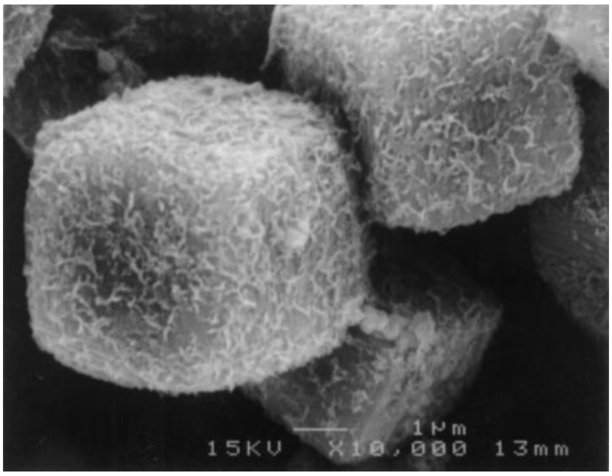

Fig. 19 SEM of particles consisting of Mn cores coated with Ni. The original Mn_2O_3 cubes coated with a shell of NiO were reduced in a stream of hydrogen for 6 h at 350 °C.[58] (Reproduced by permission of the American Chemical Society)

Table 3 Mean particle length (l), axial ratio (R), specific surface area (A_8), crystallite size (L), Fe content, SiO_2 content, coercivity (H_c), saturation magnetization (σ_s) and squareness (S) of iron particles prepared by reducing hematite powders with hydrogen at 400 °C

								VSM (CU)[a]			BM (R-P)[a]			VSM (R-P)[a]		
Sample	Precursor α-Fe_2O_3	l/μm	R	A_8/m^2 g^{-1}	L/nm	Fe/wt%	SiO_2/wt%	H_c/Oe[b]	σ/emu g^{-1}	S	H_c/Oe	σ_s/emu g^{-1}	S	H_c/Oe	σ/emu g^{-1}	S
I	Pure hematite	0.49	8	18 [26][c]	60	95	0	680	130	0.30						
II	Silica-coated	0.49	8	57 [23]	32	93	1.5	910	140	0.37	1042	115	0.47	972	118	0.45
III	Silica-coated	0.38	7	51 [35]	22	93	1.3	1070	110	0.49	1328	108	0.52	1248	112	0.50
IV	Silica-coated	0.29	6	52 [40]	30	93	1.5	930	140	0.42	1136	114	0.49	1058	118	0.49
V	Silica-coated	0.22	5	65 [43]	<5	85	2.1	890	100	0.48	905	120	0.50	839	123	0.48
VI	Silica-coated			20	50	73	0	775	170	0.32	608	148	0.43	250	154	0.43

[a] Measurements with the vibrating sample magnetometer at Clarkson University [VSM (CU)] and at Rhône-Poulenc [VSM (R-P)] and with the BM meter at Rhône-Poulenc [BM (R-P)]. [b] Oe = 79.6 A m^{-1}. [c] In brackets are the specific surface area of precursor particles before reduction.

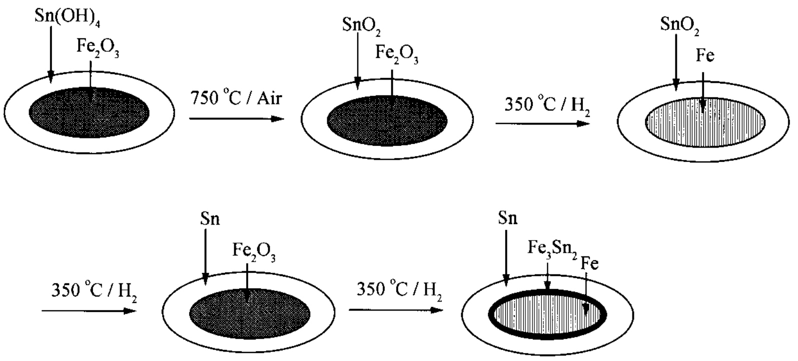

Fig. 20 Schematic presentation of various phases in the reduction of α-Fe_2O_3 particles coated with SnO_2 in hydrogen at 350 °C.[59] (Reproduced by permission of Steinkopff Verlag)

silica can be deposited on particles to form a protective layer, as was done on iron, [53,54] copper basic carbonate or copper particles,[42] and on a ruthenium complex compound.[55]

The core of silica-coated metal compounds could then be reduced with hydrogen gas to metals at elevated temperatures under conditions that depended on the investigated system. Fig. 17 shows electron micrographs of the original silica-coated hematite and of the same particles after reduction with hydrogen.[56] After the calcination/reduction process the resulting iron is protected by the silica shell, which becomes impermeable to gases. The magnetic properties of the final powders depend on the weight ratio $SiO_2 : Fe$.[56] Analogous results were obtained with iron particles on which the silica shell was produced from Na_2SiO_3.[48] Table 3 lists magnetic parameters as determined by different techniques in two laboratories for several samples of varying size and $SiO_2 : Fe$ ratios.[48]

Both copper(II) basic carbonate and copper(II) oxide coated with Ludox silica particles could be reduced to pure metal. The coating was especially important in the case of copper(II) basic carbonate, because without the protective layer, the particles disintegrated on heating. In another example, CuO particles coated with $Y(OH)CO_3$ broke up at higher temperature.[42] Apparently, hydrogen gas and water vapor could not freely permeate through the shell, causing the fragmentation.

Amorphous spherical particles of a rather complex composition were obtained by aging solutions of ruthenium chloride (K_2SO_4) and urea.[55] These powders could be converted to RuO_2 by calcination at 400 °C, which in turn yielded metallic ruthenium when heated at 250–300 °C in a stream of hydrogen. Again, to preserve the spherical morphology, particles were coated with silica. X-Ray diffractograms in Fig. 18 confirm the described transformation.[55]

Reduction of cores and coatings. Recently, uniform cubic manganese carbonate particles were produced by homogeneous precipitation in aqueous solutions of manganese sulfate and urea at elevated temperatures.[57,58] These cubes were then dispersed in solutions of nickel sulfate and urea and aged at 80 °C, which produced a shell consisting of the hydrated double salt $NiCO_3 \cdot Ni(OH)_2$. On calcination of the resulting powder the cores and coatings transformed independently into NiO and Mn_2O_3. Finally, heating this powder at 350 °C in a stream of hydrogen caused a reduction to Mn and Ni. Fig. 19 illustrates the so-obtained manganese particles covered with nickel. As one would expect the surface is quite rough due to the decomposition of the original carbonate and/or hydroxylated cores and shells.

In another system it was possible to produce a tin coating on iron, which in itself is an interesting case. First, ellipsoidal hematite (α-Fe_2O_3) particles were dispersed in an acidic solution of $SnSO_4$ and urea, which on heating at 80 °C, produced an amorphous tin hydroxide shell on these cores. Calcination at 750 °C of this powder changed the composition of the outer layer to SnO_2, and on further reaction with hydrogen at 350 °C the final coated particles consisted of Fe, Sn and Fe_3Sn_2.[59]

It is noteworthy that SnO_2 powder prepared under the same conditions in the absence of hematite could not be reduced by hydrogen to pure metal. This finding led to a mechanism for the processes involved in the formation of Fe/Sn coated particles, as given by the following reaction steps:

$$Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O \tag{8}$$

$$4\ Fe + 3\ SnO_2 \rightarrow 2\ Fe_2O_3 + 3\ Sn \tag{9}$$

$$Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O \tag{10}$$

According to this mechanism, H_2 permeates through the tin oxide shell and reduces the hematite core, which in turn reduces SnO_2 to Sn. The produced iron oxide is again converted to the metal by hydrogen, until the entire powder is in the metallic state. At the interface between Fe and Sn, a small amount of the alloy Fe_3Sn_2 is formed. The entire process is schematically illustrated in Fig. 20.[59]

Acknowledgements

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