



Review

Strategies for tailoring the properties of chemically precipitated metal powders



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ABSTRACT

This review discusses the fundamental principles governing the precipitation of metallic particles in liquid media and describes practical strategies for controlling their size, shape, uniformity, dispersion, composition, structure, and surface characteristics. The manuscript covers theoretical and practical aspects applicable to both small-scale laboratory systems and large-scale industrial processes. The review focuses mainly on the latter to compensate for the sparse coverage they receive in the literature despite their significant impact on various technology fields. For this reason, the majority of examples given to illustrate the validity and effectiveness of the strategies described pertain to high volume/high concentration systems for manufacturing metal powders for industrial applications.

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1. Introduction

Metallic particles are widely used in metallurgy [1–3], electronics [4–6], optoelectronics [7–9], catalysis [10–15], biosensors [16, 17], Surface Enhanced Raman Scattering (SERS) [18–22], and biomedical applications [23–28]. In principle, three different approaches can be used to generate finely dispersed metals [29]. The ‘phase breakdown’

(or ‘top down’) involves the use of external energy to divide the liquid or solid bulk metal into small entities with high specific surface area. In the first case, the molten metal is dispersed through various means (pneumatic, spinning disk [30, 31]) into small droplets which are then rapidly cooled. Depending on the nature of the metal, this process is conducted in air or controlled atmosphere (inert, reducing). The resulting particles are typically spherical/spheroidal, very large (tens to hundreds of micrometers), and have very broad size distributions. Consequently, their use is limited mostly to metallurgical applications. When the metal is in solid form, the external energy necessary for size reduction is supplied via

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milling processes [32] involving the action (impact, shear) of small objects (usually spheres) made out of hard materials. Although soft metals are not suitable for this process, some (i.e. silver) become brittle at very low temperature and can be eventually crushed (cryogenic milling [33, 34]). The size reduction can be conducted in various types of equipment (ball mill, attritor, etc.) in either gas or liquid media. Depending on the metal's properties, a controlled atmosphere may be required as well. The milling process can yield particles down to hundreds of nanometers or less but fails to provide tight size distributions and particle shape control. Despite these disadvantages, this approach is widely used in the manufacturing of metal powders and flakes (Ag, Au, AgPd, Cu, and Ni) for the electronic industry [35].

The second route ("phase transformation") consists of converting finely divided metal compounds into metal particles [36]. The transformation can be achieved through thermal decomposition (i.e. pyrolysis) [37–40], chemical reduction, or a combination of the two. The approach is particularly useful in the preparation of anisotropic metallic particles as often it is easier to prepare particles of metallic compounds with unique shapes [41]. When the conversion takes place at high temperature, the process can yield highly crystalline metal particles and, for multi-elemental systems, alloy powders. Chemical transformations can be conducted in both gas and liquid dispersion media at either ambient or elevated temperatures. However, the phase transformation in liquid phase is limited by the boiling point of the dispersion medium and the partial dissolution of the precursor salt can become a complicating factor.

In the "phase build-up" ('bottom up') approach the metal atoms are used as building blocks. The generation of the latter and their assembly into the final particles can be carried out in either gas phase (chemical, physical vapor deposition [42–44]) or liquid media (chemical precipitation [45–49]). Although the two methods are similar in principle, the difference in the dispersion medium gives each route specific advantages. As the build-up in the gas phase proceeds at high temperatures, it results in highly crystalline metallic particles. However, the inability to prevent inter-particles collisions leads to severe aggregation and/or loss of particle uniformity and shape control. In contrast, the "phase build-up" in liquid dispersion media (chemical precipitation) provides a better control of the particle formation mechanisms and inter-particles forces. In this case it is possible to control the size of the final particles (through the number of atoms incorporated), their shape (by controlling the attachment of ad-atoms to different crystal facets), and composition (through selection of elements precipitated). The ability to control the aggregation of smaller particles into larger polycrystalline entities allows also adjustments of the internal structure of the particles [7, 9, 48]. Lastly, the surface properties of the particles can be tailored by employing a wide variety of solvents, dispersants/surfactants, and other ionic and molecular species. An important merit of the chemical precipitation is that such sophisticated control of particles properties can be achieved at low cost on large scale. Its significant limitation, however, is the inability to reduce highly electronegative metals in common solvents and ordinary conditions.

2. Mechanism of metallic particle formation in liquid media

Although methods in which the metal atoms are formed 'ex-situ' and then assembled inside the liquid dispersion medium are known [50, 51], this review deals only with the case in which they are generated in the liquid phase as a result of redox reactions. Without minimizing the merit of the former approach, it is easy to understand how the ability to manipulate the reactivity of oxidized metallic species and the electron transfer enhances the control of atoms generation in the system and the thus the properties of final particles.

In chemical precipitation, the metal atoms are formed by reacting oxidized metallic species in form of ions or molecules with compounds with reducing capabilities (reductants) (Eq. (1)).



Where:

n	is oxidation number ($n = 1, 2, 3, \dots$)
Me^{n+}	symbolizes the oxidized metallic species
Me^0	stands for the metal atom
Red	stands for reducing agent
Ox^+	represents the oxidized form of reducing agent

The driving force behind the process is the redox potential of the overall reaction (ΔE), the value of which must be positive in order for the electron transfer to be thermodynamically possible. A higher positive value of ΔE translates in a more negative value of the Gibbs free energy, and, thus, a higher probability for the reaction to occur (Eq. (2)).

$$\Delta G = -nF\Delta E \quad (2)$$

Where:

ΔG	stands for Gibbs free energy,
n	is the number of electron transferred,
F	is Faraday's constant

It is generally accepted that a larger Gibbs free energy favors an increased rate of atoms generation. This leads to the formation of a larger number of nuclei and, as it will be shown later, smaller final particles. Due to their exceedingly high energy, the metal atoms easily associate into clusters as their concentration in the solvent increases. The clusters can still dissociate back to free atoms and, as such, cannot be considered yet a stable metallic phase. As the concentration of metal atoms increases, a critical radius (R^*) is eventually reached. Clusters with radius larger than R^* keep growing through addition of more atoms and become stable. These entities (nuclei) represent the first stable solid metallic entities in the liquid dispersion medium. According to the LaMer model [52–55], the nucleation process is driven by the supersaturation (S) of free atoms in the system, defined by Eq. (2).

$$S = C/C_{\text{eq}} \quad (3)$$

Where:

C	actual metal atoms concentration
C_{eq}	solubility of the metal in the given system

Fig. 1 represents the change in the concentration of solute metallic atoms in the precipitation process. The supersaturation builds up from A to B. Once the concentration of metal atoms reaches the critical supersaturation, S_c , nucleation occurs (point B). It is typically a very rapid process ('burst') followed by a rapid depletion of the solute atoms until their concentration decreases to the saturation concentration of the metal in the respective solvent (C_{eq}). As long as the concentration of the solute atoms does not exceed again the supersaturation level, further nucleation bursts are not possible. During the following 'supersaturation release' the nuclei grow rapidly from less than 0.8 nm (20–30 atoms) to 'primary particles' of a larger size. Depending on the system conditions, the later can be as small as 1.0 nm and as large as 30 nm. During their growth the primary particles are inevitably the subjects of attractive (Van der Waals) and repulsive (electrostatic) forces. If the repulsive forces prevail throughout the 'supersaturation release,' the primary particles form a stable colloidal system in which the unique properties (optical, electronic, transport etc.) that are essential in

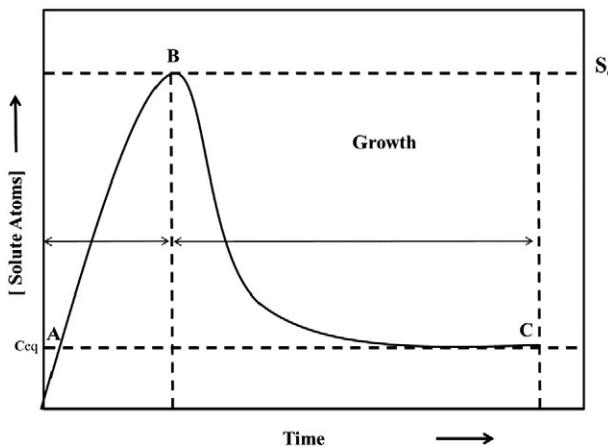


Fig. 1. The variation of the concentration of metal atoms with time in the precipitation process [52].

many applications are preserved. Conversely, the primary particles aggregate if the attractive forces overcome the repulsive forces. The balance between repulsive and attractive forces affecting these processes depends on many factors (solvent dielectric constant, nature precipitated metal, counterions charge and concentration, etc.), which are discussed elsewhere [56, 57].

The primary particles continue to grow if metal atoms are continuously generated in the dispersion medium. However, to prevent subsequent nucleation bursts that can lead to polydispersed systems, it is essential that the supersaturation limit is not exceeded. In principle, particle growth can proceed through two distinct mechanisms: diffusional growth and aggregation. The first relies on the diffusion and deposition of atoms to the surface. Since the orderly arrangement of the ad-atoms require a finite time, the diffusional growth is typically slow. Alternatively, the primary particles may aggregate to form much larger entities. This process is usually rapid and occurs when the balance between the attractive and repulsive forces is suddenly tilted in favor of the former. The internal cohesion of the resulting large aggregates requires that aggregation overlaps to some extent with diffusional growth so that the primary particles are ‘fused’ together following the deposition of ad-atoms at the contact points. The diffusional deposition can even fill spaces in the arrangement of primary particles to yield particles with density approaching that of bulk metal. Particles formed predominantly by one of these two growth mechanisms have very different internal structures. Those obtained by diffusion growth typically have few internal grain boundaries and can adopt well defined regular shapes (cubes, prisms, platelets, rods, etc.). In contrast, the particles formed by aggregation of a large number of smaller crystallites are in general spherical and have smooth surfaces. It must be noted that by changing the reaction conditions particles of intermediate ‘polycrystallinity’ can be prepared as needed. This becomes extremely important when designing metallic particles for specific practical applications. Fig. 2 reflects the entire sequence of events from the reduction of metal ions to the formation of large metallic particles with different internal structure.

3. Controlling the properties of metallic particles

3.1. Particle size

The size of the particles is a critical parameter in most, if not all, applications relying on finely dispersed metals. The importance of this parameter in catalysis, electronics, metallurgy, pigments, etc. has been amply documented and the need to control the physical dimensions of particles widely recognized.

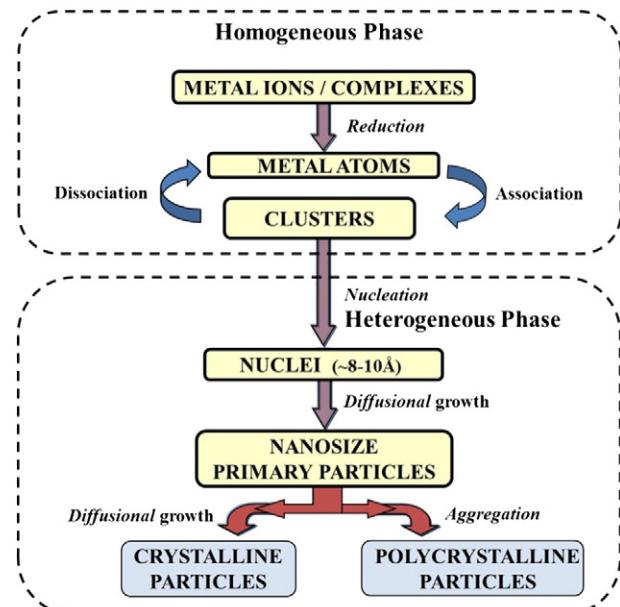


Fig. 2. Schematic presenting the key stages in the precipitation of metallic particles.

3.1.1. Redox potential as controlling parameter

Manipulating the ΔE of the redox reaction is perhaps the most effective way to control particle size. As previously stated, a large value causes a more rapid supersaturation buildup and leads to the formation of a larger number of nuclei. Conversely, a small ΔE gap generates fewer nuclei. For the same amount of metal reduced, it is obvious that smaller final particles will be formed in the first case. The most effective and practically facile way to adjust the redox potential of the reaction is through the selection of reducing agent. Strong reducing agents (i.e. sodium borohydride [58–60]) as well as milder ones (ascorbic acid [61–68], alcohols/polyols [69–74], sugars [48, 75], tetrahydrofuran [76]) are widely used in the chemical precipitation of metals. The compounds in the first category provide a fast generation of nuclei while those in the second group tend to favor slow reductions. If all other process parameters are the same, the former tend to generate small particles while the latter result in larger ones. Other parameters also affect the redox potential of the metal ions and/or reducing species. A change in the pH may impact not only the potential of each reactant but also that of the entire reaction [77–81]. A good example is the case of ascorbic acid. Since its reducing ability depends on the protonation degree of the molecule, an increased proton concentration (lower pH) translates in a diminished ability to transfer electrons to the metallic ions and thus slower reductions [29, 82]. Similarly, the redox potential of hydrazine becomes more negative at higher pH (-1.16 V in alkaline conditions vs. -0.26 V in acidic medium) due to the fact that OH^- are consumed in the oxidation of N_2H_4 to elemental nitrogen [83]. Thus, hydrazine can be rendered mild or strong reductant by varying the pH of the reaction environment. Complexation is another effective tool in controlling the redox potential of oxidized metallic species. As a rule, engaging the metal ions in progressively stronger complexes decreases gradually their redox potential and makes their reduction more difficult. The complexation of silver ions with various ligands is a good example. While the standard redox potential (E^0) of the Ag^+/Ag^0 system is $+0.799$ V, that of the $\text{Ag}[(\text{NH}_3)_2]^+/\text{Ag}^0$ pair is $+0.373$ V and of AgCl/Ag^0 is $+0.222$ V [29]. As a result, when using the same reductant and experimental conditions the precipitation of silver becomes more difficult in this order. Sometimes OH^- ions can be the complexing species, case in which an increase in pH affects simultaneously the redox potential of both the reductant and metallic species. For example, the substitution

of Cl^- ions with OH^- in the $[\text{AuCl}_4]^-$ complex following the addition of a NaOH decreases the redox potential of the latter from +0.71 to +0.60 V [84]. When all these parameters (standard redox potential of Me^{n+} ions, pH, and complexing agents) are considered when designing the precipitation process, it is possible to significantly alter the reaction redox potential of a given redox system and thus obtain particles with a broad range of sizes.

3.1.2. Surfactants and dispersants

While the main role of these additives is to prevent the aggregation of metallic particles or impart specific surface characteristics (aspects discussed latter), they can also affect particle size. For example, in the case of the reductions conducted in reverse micelles the amount of metal incorporated in one particle is dictated by the size of the micelles, which depends on the type of surfactant used [85–91]. The dispersant plays an important role in the nucleation and growth of particles as well [52, 92–94]. Typically, when the concentration of the dispersing agent increases, the particle size tends to decrease and the uniformity improves. The former effect is due to the generation of an increased number of nuclei in a given volume. The second is simply a consequence of the smaller size. It is noteworthy that certain reducing agents can have a similar effect. When citrate molecules [95–97] or organic amines [98, 99] are used in the synthesis of Au nanoparticles, they do not only provide the electrons needed for the reduction but also favor the formation of very small metallic particles.

3.1.3. Seeding

An effective way to control the size of metallic particles is through heterogeneous nucleation. In this case, small metallic particles are either added in the system or generated "in situ" before the reduction of the metal starts. Because of their catalytic properties, noble metals (Pd, Pt) are frequently used as 'seeding' agents in the synthesis of more electronegative metals (Ni, Cu, Co, Fe, etc.) [100, 101]. Fig. 3 shows images of dispersed isometric Ni particles formed in the polyol process in the presence of different concentrations of tetrachloropaladate ions ($[\text{PdCl}_4]^{2-}$). The seeding element may be the metal that is deposited or

a different one. When the seeds are different from the precipitated metal, the epitaxial growth is possible only when the two elements have similar lattice parameters. This scenario, called hetero-epitaxial growth, is applicable to the Ni/Pd polyol process illustrated in Fig. 3 but can be equally effective in aqueous systems [102–106].

3.2. Particle shape

The ability to control particle morphology has been left far behind the capabilities achieved in controlling their size. This is particularly frustrating as the properties of the final particles (optical, catalytic, transport, packing characteristics, adhesion, etc.) depend to great extent on their shape. To date, the shape selection mechanisms proposed have dealt mostly with specific shapes and restrictive experimental conditions. As a result, their applicability to other systems is limited. In principle, the shape of precipitated particles can be determined at any stage of their formation. During nucleation, the atoms comprising the supersaturation are associating in increasing number until the critical size of the dynamic embryos reaches the critical radius R^* (see proceeding section). If the generation of atoms in the dispersion medium is very slow, the association of atoms may lead to anisotropic nuclei due to the difference in the energy of different crystal facets [47]. Once such entities are formed, they may continue to grow along preferential directions during the supersaturation release stage yielding larger anisotropic primary particles. In contrast, if the supersaturation concentration is high and the nucleation rapid, the nuclei tend to be isometric (i.e. spherical), as the ad-atoms do not have time to discriminate between various crystal facets. As this situation is preserved during the rapid "supersaturation release," the resulting primary particles remain essentially isometric. As the rate of atom generation in the liquid phase is controlled by ΔE , the most obvious approach to control particle shape is through a suitable selection of complexing agents and/or reductants used. Indeed, precipitations involving very stable metal complexes and/or mild reducing agents (i.e. narrow ΔE) are more likely to yield anisotropic entities.

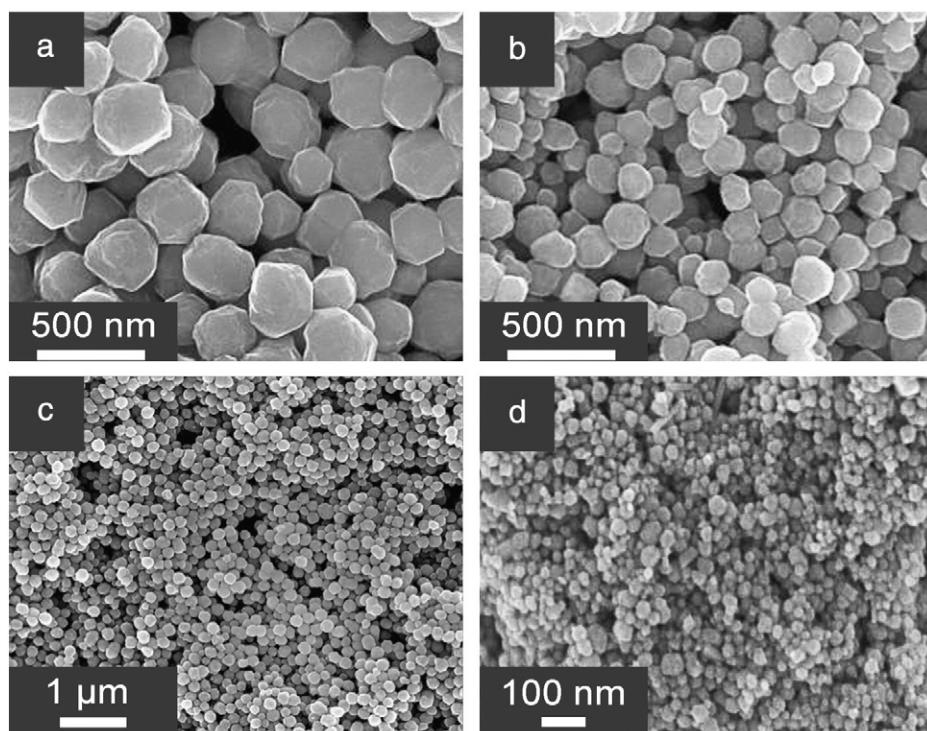


Fig. 3. Dispersed Ni particles of different diameter precipitated in boiling propylene glycol process in the presence of different amounts of Pd (added as $[\text{PdCl}_4]^{2-}$ ions): a) 0 ppm Pd; b) 100 ppm Pd; c) 1000 ppm Pd, and d) 2500 ppm Pd.

The surface energetics plays an important role in particle growth and shape selection. Precious metals (Ag, Au, Pd, and Pt) have a face centered cubic (*fcc*) crystal structure. For this type of crystal, the surface energy of (111) facets is lower than for (100) and (110) [107–109]. Wulff polyhedrons contain extended (111) facets and are therefore often incorporated in the structure of noble metallic particles [52, 110–112]. Since this type of crystal habitat maximizes the expression of (111) facets, systems in which such entities are present are more prone to anisotropic growth. Structural defects (twin or multi-twin platelets) generated in specific system can have an important role as well in shape control. It has been reported that nitric acid is a critical factor contributing to the formation of Ag nanoplatelets during the reaction of silver nitrate with ascorbic acid [47]. When nitric acid is present in high concentration, it creates a strong oxidizing environment in which metal atoms are re-oxidized (and thus removed) preferentially from high energy facets. The combination of this effect and the deposition of the silver at the lower energy facets lead to preferential growth along the (111) planes [113, 114] and formation of platelets (Fig. 4).

One element that can contradict the shape predictions based on the reduction rate and surface ‘energetics’ is the ‘template’ effect. In this case, ions, surfactants, and dispersing agents direct preferentially the atoms at particular locations [65, 66, 93, 115–121]. These species are even more effective when paired with relatively weak reducing agents that provide a slow growth. Polyols, for example, have been used successfully to control particle morphology either by themselves or in combination with such compounds [113, 122–125]. A relevant example is the formation of silver wires during the reduction of AgNO_3 in ethylene glycol in the presence of polyvinylpyrrolidone (PVP) and tetrabutylammonium chloride (TBAC) (Fig. 5a). In some cases, however, the growth directing agents are effective even in the cases of relatively fast reduction rates. It was recently shown that naphthalene sulfonate formaldehyde copolymers facilitate the formation of Ag wires in the case of the rapid reduction of silver nitrate with ascorbic acid in acidic solutions [121]. The decrease in the solubility of the dispersant due to the protonation of the sulfonic groups leads to the formation of extended lamellar structures along which the silver wires grow rapidly (Fig. 5b).

In some cases, a seed-mediated growth method can be combined with the template effect [65, 66, 93, 116, 118, 128, 129]. A common route in the preparation of Ag platelets is to first form metallic seeds by reducing Ag ions with a strong reducing agent (i.e. NaBH_4) followed by a step involving a weaker reductant [93, 130]. In the second step the selective adsorption of an ion or a capping agent can alter the growth mechanism. It has been reported that halide ions play a significant role in the morphology of final particles [131–133]. Mirkin et al. [131] reported that I^- ions preferentially adsorb on the (111) and (110) facets of Au nanoparticles and act as growth-directing moieties. By varying the concentration of I^- alone, the morphology of the Au nanoparticles can be changed from spheres, to rods, and to prisms in the presence of cetyltrimethylammonium bromide (CTAB). Similarly, Br^- ions can

selectively adsorb onto (100) facets of Ag, Au, and Pt nanocrystals with edge length less than 25 nm and promote the growth of nanocubes, rectangular nanobars, and octagonal nanorods [113, 134]. Selective adsorption of surfactant (capping agents) on different crystal facets can also promote anisotropic growth. Although the effect is more pronounced for larger molecules, small ones (i.e. citrate [130]) can be effective as well. Polyvinylpyrrolidone (PVP) is one of the most commonly used capping agents in controlling particle morphology. The oxygen atoms in the PVP molecule have a strong interaction with the (100) facet of Ag nanocrystals [115, 122, 135–138]. The growth in this direction is thus inhibited while the (111) and (110) facets remained favorable to the addition of Ag atoms. Ag nanocubes, nanowires, and nanorods have been synthesized following this approach. As already mentioned, CTAB is also used as a capping agent and promotes the formation of nanorods, nanofibers, and nanoplatelets [93, 128, 139]. For the formation of silver nanoplates, it has been accepted that the CTAB preferentially adsorbs on the (111) plane of the silver seeds [93]. Besides the selective adsorption mechanism, another growth mechanism (template mechanism) has been proposed to explain the formation of silver nanowire/nanotube in the presence of CTAB as a capping agent [128]. In this case a capping agent containing hydrophobic and hydrophilic groups forms micelle structures which act as templates for growth. The morphology and size of the particles inside of the micelle are determined by the type of micelles formed.

To further complicate the situation, particles of well-defined geometric shapes can be formed by aggregation of smaller isometric entities. These particles appear at low magnification as regular crystals of various shapes but when investigated by electron microscopy at higher magnification they clearly show the presence of subunits. The polycrystalline nature can be further substantiated by XRD, the crystalline size determined by the Scherrer's equation [140] being much smaller than the actual particle size [141]. The copper particles shown in Fig. 6 are the good illustration of this case. At low magnification, they look as perfectly shaped crystals (Fig. 6a) but both SEM inspection at higher magnification (Fig. 6b–d) and XRD analysis reveal that they consist in fact of aggregates of smaller crystallites.

3.3. Internal particle structure

Depending on their formation mechanism, metallic particles can have different internal crystalline structures. While in all cases the lattice (spatial atoms arrangement) remains the same, the entire particle can have either a highly crystalline structure (i.e. extended orderly arrangement of atoms) or polycrystalline (consisting of many joined small crystalline domains). As suggested by the general formation scheme given in Fig. 2, highly crystalline particles form when the primary particles grow by a slow diffusion of ad-atoms to the surface. In contrast, polycrystalline particles form when small primary particles (crystallites) aggregate rapidly. These drastically different formation mechanisms imprint significant morphology and surface topography

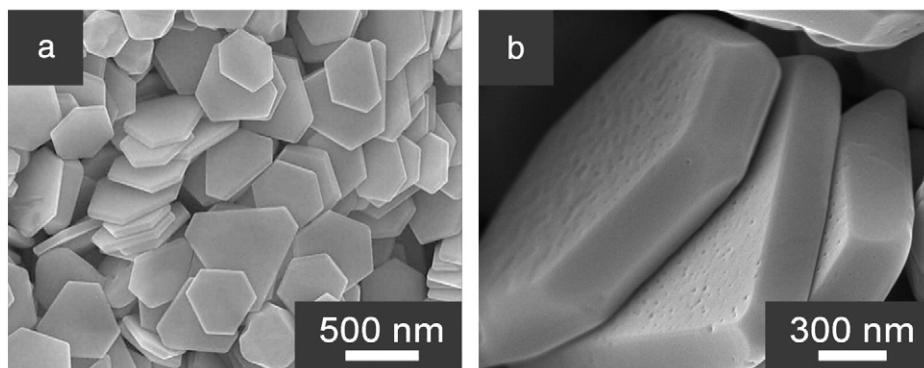


Fig. 4. Silver (a) and silver/palladium platelets prepared by reducing the respective metal nitrates with ascorbic acid in 10% wt.% HNO_3 in the presence of Arabic gum.

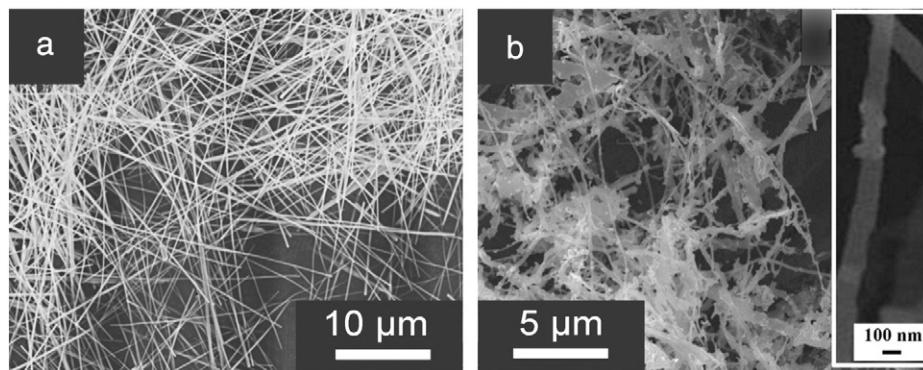


Fig. 5. Silver wires formed by: a) reduction of silver nitrate in ethylene glycol in the presence of PVP and TBAC [115, 126, 127] and b) reduction of silver nitrate with ascorbic acid in the presence of Daxad 11G [121].

varyations that can be easily detected by electron microscopy. Indeed, as illustrated in Fig. 7, the former display extended flat facets while the small constituent crystallites in the latter make them appear as well-shaped, smooth spheres. The crystalline structure can be accurately assessed by XRD analysis using the Scherrer's equation, which estimates the crystallite size (the smallest domain in the particle with a highly ordered crystal structure).

The internal structure of metallic particles plays a major role in many applications. In electronics, for example, the densification (firing) of packed deposit of particles leading to conductive lines/structures is greatly influenced by crystallinity. Highly crystalline particles sinter rather slowly (due to only inter-particle mass transport) and form dense, continuous, and highly conductive structures. Polycrystalline particles on the other hand, are less desirable in such cases as the “intra-particle” sintering complicates the sintering/densification of the metal, often leading to less continuous layers. They are, however, well suited for other situations. For example, in the case of the formation of the silver conductive grid on the front side of crystalline silicon solar cells, highly polycrystalline spherical Ag particles perform better as

they sinter rapidly and completely in the short time the wafers are kept at a relatively low temperature ($780\text{--}830\text{ }^{\circ}\text{C}$). The ability to tailor the size of metallic particles is essential for both types of particles. While the strategies outlined in Section 3.1 are all relevant for the preparation of crystalline particles, in the case of polycrystalline particles the final size can also be controlled through the size and number of nanosize primary crystallites incorporated. The former can be adjusted by tailoring nucleation while the latter by controlling the experimental conditions affecting the aggregation process (ionic strength, pH, amount and nature of dispersant, etc.). Fig. 8 shows polycrystalline silver particles of different sizes obtained following the latter strategy.

3.4. Particle composition

Precipitation in homogeneous solutions can be used to prepare particles containing more than one metal. To do so, all components must be quantitatively reduced in a given set of experimental conditions. In the simplest case of bi-metallic particles, two outcomes are possible. If the E° of the two metals is similar and their reduction is rapid (i.e. reactive

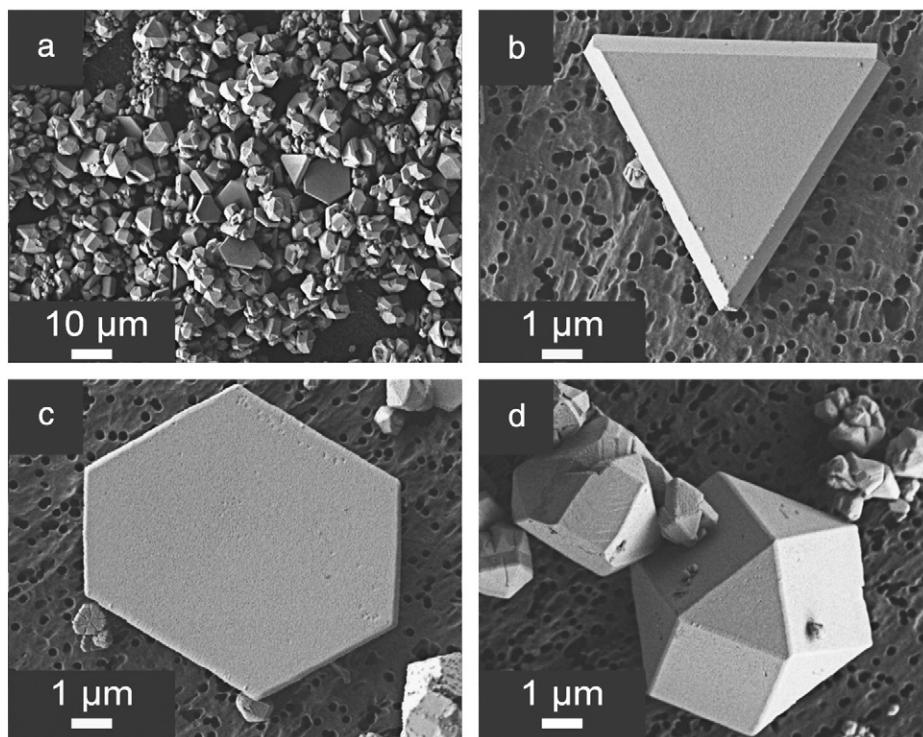


Fig. 6. Copper particles formed by reducing copper sulfate with ascorbic acid in diethylene glycol at $170\text{ }^{\circ}\text{C}$ in the presence of Daxad 11G as dispersant (unpublished data).

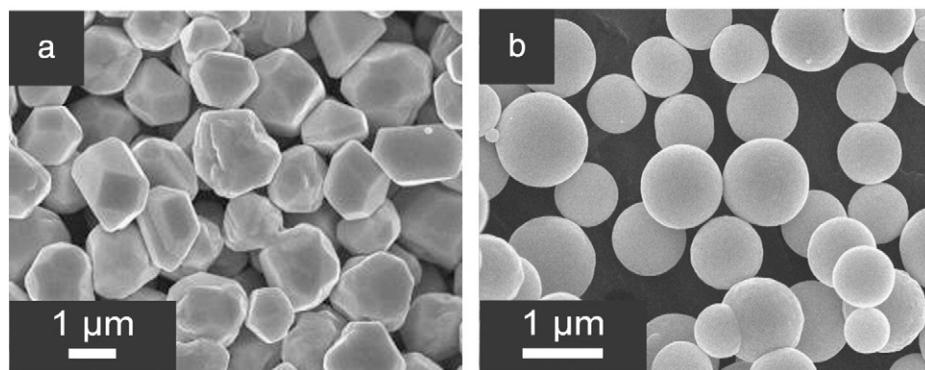


Fig. 7. Dispersed silver particles with different internal structure: a) highly crystalline particles prepared by reducing slowly silver nitrate with ascorbic acid in a dilute nitric acid solution; b) highly polycrystalline particles prepared by reducing rapidly an Ag polyamine complex with ascorbic acid at pH 10.0 [49].

metallic species paired with strong reducing agents), particles with an alloy structure can be obtained. If the E^0 values are significantly different, core-shell structures are typically formed as the more electro-positive metal forms the core while the more electronegative one is reduced slower and forms the shell [32]. Fig. 9 shows examples of core-shell and alloy AgPd particles with the same size, shape, and composition (70 wt.% Ag, 30 wt.% Pd) obtained by changing the conditions of the chemical precipitation.

Since the redox potential E^0 of individual metallic species can be altered by complexation or precipitation (Section 3.1.1.), it is possible to reverse the order of reduction and, thus, the particle structure. Core-shell structures can also be obtained by the “seeding” approach in which both the core and the shell metals can be deposited in a more controlled manner by sequential precipitation. Such particle structures have great importance in electronics, catalysis, sensors, medical applications, etc.

3.5. Particle uniformity

Particle uniformity affects most properties of colloidal metals. For plasmonic elements it impacts the optical properties (critical in decorative and sensing applications [142, 143]) as well as the release of drugs adsorbed on their surface as a result of excitation with electromagnetic

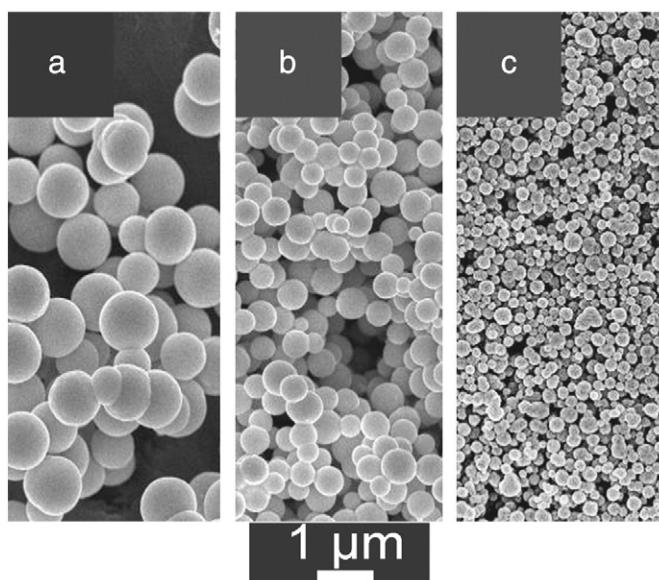


Fig. 8. Polycrystalline Ag spherical particles obtained by reducing a silver amine complex with ascorbic acid in a) 100% water ($\sim 1.0 \mu\text{m}$), b) 95% water/5% DEG ($\sim 400 \text{ nm}$) and c) 75% water/25% DEG ($\sim 100 \text{ nm}$). In all cases the crystallite size estimated with the Scherrer's equation is $\sim 14 \text{ nm}$ [49].

radiation [25, 144]. The stability of metal dispersions (inks and pastes) is also affected by the uniformity of particles. Indeed, aggregation of smaller particles and rapid settling of the larger ones are detrimental to dispersion stability. In electronic applications particle uniformity is also essential for obtaining densely packed green structures that yield continuous, defect-free structures after sintering [145, 146]. Controlling the uniformity of the particles means not only that the mechanisms involved in particle formation are well understood but also that all critical stages of the precipitation process are tightly controlled. To prepare uniform nanoparticles one must ensure that a single nucleation burst occurs and the formed nuclei and the growing particles remain dispersed throughout the entire process. Fig. 10 shows images of highly uniform dispersed gold and silver nanoparticles prepared following this strategy [48, 146].

Obtaining uniform large metallic particles is more challenging. Generally, as the particles reach sub-micrometer and micrometer

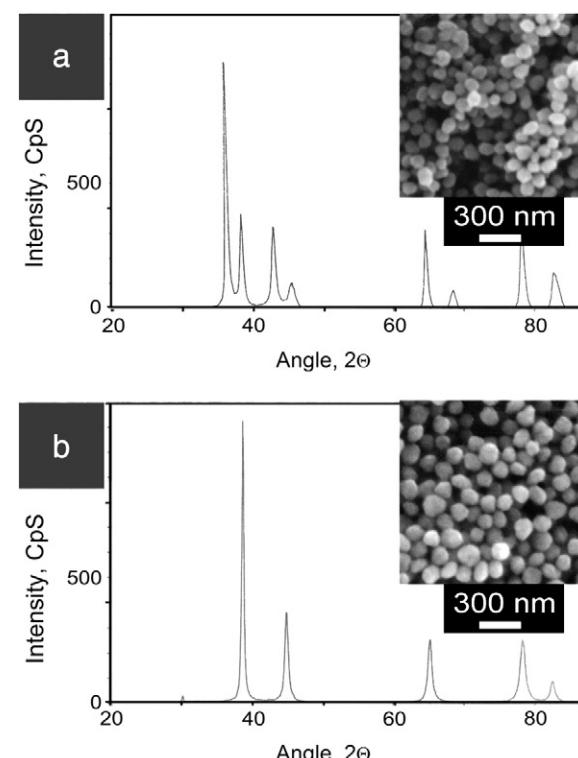


Fig. 9. XRD patterns and SEM images of: (a) core-shell AgPd particles ($\sim 130 \text{ nm}$) obtained by adding hydrazine hydrate solution to a silver/palladium ammonia complex solution containing Arabic gum; (b) alloy AgPd particles ($\sim 140 \text{ nm}$) prepared by adding ascorbic acid to a solution containing silver nitrate, palladium nitrate, nitric acid, and Arabic gum.

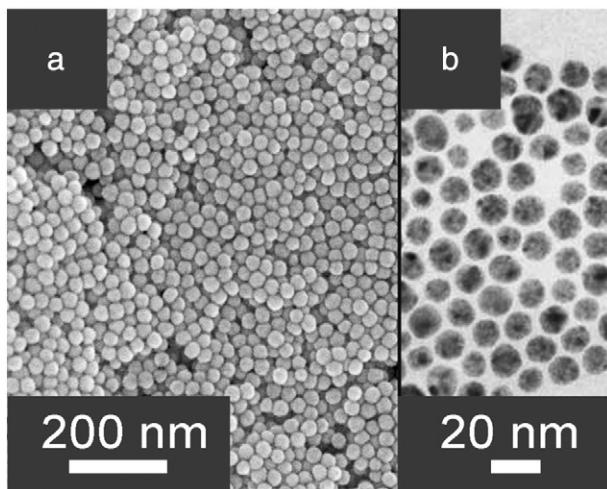


Fig. 10. a) Uniform gold nanoparticles (~ 20 nm) prepared by reducing gold chloride with diethyldiaminodextrane [48]; b) uniform 12 nm silver particles prepared by reducing silver salicylate in polyol in the presence of Daxad 11G as dispersant [147].

dimensions they become less uniform. For large crystalline particles the difficulty in preserving uniformity arises from the increased probability of inter-particles collisions during extended reaction times. In the case of polycrystalline particles, it depends on how uniformly the aggregation centers are generated in the reaction volume. Since this is affected by concentration gradients of reactants and additives in the reaction volume, the addition rate of reactants and mixing are important parameters in chemical precipitation processes.

3.6. Particle dispersion

An excellent dispersion of metallic particles is necessary in order to display unique optical properties (in the case of nanoparticles) or for

optimum performance in various other applications. The effect of particle dispersion on optical properties has been extensively studied and demonstrated in numerous practical applications. An excellent dispersion is also essential in electronic applications where long term stability of metallic conductive inks and the ability to print fine lines consisting of densely packed deposits of particles that form defect-free metallic structures are essential.

The aggregation of metallic particles leading to poor dispersion is a major issue in chemical precipitation. This is particularly valid for non-aqueous processes (where the electrostatic repulsive forces arising from the charged double layer are weak) and in concentrated systems (where the electrical double layer responsible for electrostatic repulsive forces is greatly compressed). Certain dispersion media are more effective in screening the attractive forces than others. When metals are prepared by reduction in polyols (ethylene glycol, 1,5-pentanediol, diethylene glycol, etc.), for example, the particles remain dispersed at higher metal concentrations than in water [52, 148]. The higher viscosity of these compounds and the ability of their molecules to form hydrogen bonds at high temperature are likely the reasons for their superior ability to prevent particle aggregation. Using metallic salts containing anions that do not contribute to an increase in the ionic strength permit the preparation of dispersed metallic particles at even higher concentrations. Using this approach, dispersions of non-aggregated Cu particles with metal concentrations as high as 20 wt.% can be obtained by the polyol process when using copper carbonate instead of sulfate, chloride, or nitrate, while still maintaining an excellent dispersion and particle uniformity (Fig. 11a,b). In aqueous systems, however, particle aggregation at high metal concentration can be avoided only by introducing in the system surfactants/polymers that ensure dispersion stabilization through either steric or electro-steric mechanisms [59, 85, 149–151]. Natural [152–154] and synthetic [117, 135, 136, 155] polymers have been used successfully for this purpose. Fig. 11c,d shows images of highly dispersed uniform polycrystalline silver particles prepared in such conditions [84, 156, 157]. To be effective, these additives must be optimized for each specific system in terms of both structure and

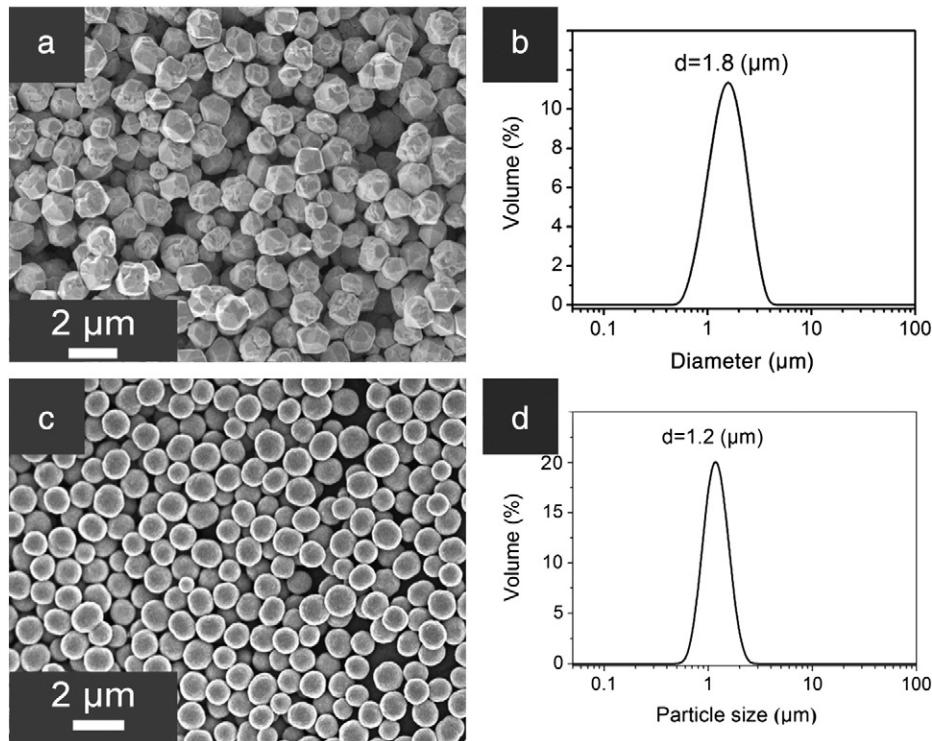


Fig. 11. a, b) SEM image and size distribution of highly dispersed Cu crystalline particles (~ 1.8 μm) obtained without dispersant by heating copper carbonate in propylene glycol at 180 $^{\circ}\text{C}$ [157]; c, d) electron micrograph and size distribution of polycrystalline silver spheres (~ 1.2 μm) obtained in water in the presence of Arabic gum as dispersant.

quantity. Unfortunately, there are few scientifically rigorous criteria allowing us to predict the effectiveness of a compound in a new experimental setup. Most often, the complexity of the precipitation environment makes this task a frustrating, complicated, and lengthy ‘trial and error’ type activity.

3.7. Surface properties

The surface of metallic particles affects the interactions with the environment/medium in which they are placed. The solvent used in the precipitation process is largely responsible for the characteristics of the metallic surface. Water is by far the most frequently used liquid medium for precipitating metals. It is readily available, inexpensive, ecofriendly and easily dissolves most common metal salts. The literature dealing with the preparation of metallic particles in aqueous medium is vast and the phenomena involved are quite well understood. While most industrial processes are based on this approach, the hydrophilic surface of the particles obtained is not well suited for some applications. Indeed, in many cases metallic particles with hydrophobic surfaces are needed. One strategy to provide such surfaces is by introducing in the solvent surfactant molecules that attach with the polar moiety to the metal. While attractive in principle, this approach rarely succeeds in concentrated systems where the surfactants can cause phase separation and/or emulsion formation. A more practical approach is to carry out the reduction in non-aqueous liquid media. One example of such system is the polyol process discussed above. As the metallic species are reduced, the polyol is oxidized to various by-products (aldehydes, ketones) which can adsorb along with the polyalcohol molecules on the metallic surface and decrease its hydrophilic character [158]. The slightly hydrophobic surface not only provides a better wetting in non-aqueous media but also increases the oxidation resistance of electronegative metals by forming a barrier that prevents the oxygen to reach the metal. This is the main reason why copper particles prepared by the polyol method can be exposed for long time to ambient environment without oxidizing. More exotic solvents (tetrahydrofuran [159], dimethylformamide [160], etc.) can be also used for preparing dispersed metals but their applicability is limited by their toxicity, cost, and sensitivity to external environment.

Another important aspect related to the surface of the particles relates to their interaction with the external environment in applications involving high temperatures. In these cases, the particles can either react with various gasses that change their composition/properties or be the subjects of mutual interactions that lead to sintering. In the first case, reactive particles which oxidize easily when exposed to air can be encapsulated into hermetic shells that seal the surface and prevent the access of O₂ to the metal. In the second case, the sintering temperature of the metal particles can be altered by depositing external shells that either promote (low melting metals) or delay (refractory metal oxides) the mass transport between particles. These strategies can be implemented during the precipitation process (through careful selection of the solvent, reductant, dispersing agent, or inorganic additives) or during subsequent steps in the separation and purification of the particles.

4. Conclusions

The data presented illustrate the capabilities of chemical precipitation process in tailoring the size, shape, composition, internal structure, dispersion, and surface characteristics of metallic particles. The unmatched control of particle properties is achieved through an appropriate selection of the solvents, metal precursors, reducing agents, additives, and reaction conditions. As it can be carried out in a very wide concentration range, the chemical precipitation has become the most versatile approach for obtaining metallic particles with well-tuned properties in both laboratory and industrial settings.

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