Part One
Copper, Silver and Gold Nanomaterials

1

Approaches to Synthesis and Characterization of Spherical and Anisotropic Copper Nanomaterials

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1.1

Introduction

Those familiar with the literature in the field of metal nanoparticles have, for sure, many times read a sentence such as: '. . . in recent years metal nanoparticles have attracted a great interest because of their unique size-dependent properties that can be different from those of the corresponding bulk material'. At the outset of this chapter, we promise the reader that we will carefully avoid any further use of this terminology! Indeed, we must specify that, when talking about nanoparticles synthesis, characterization and key properties, it is today mandatory to assess issues related to a tight control over size, shape, crystal structure and morphological purity. Obviously, chemical composition is also critical, but important aspects in the (nano)materials science have been widely demonstrated to correlate with the aforementioned morphological/structural parameters.

One of the most challenging goals in nanoparticle (NP) research is to develop successful protocols for the large-scale, simple and (possibly) low-cost preparation of morphologically pure NPs with identical properties. Additionally, NPs should be easily stored and manipulated without losing their properties. In this context, we will try to describe comprehensively the literature which exists on the preparation of copper nanosized materials, paying attention to all of these key characteristics.

The present chapter cites more than 350 papers, and focuses specifically on nonoxidized, nonsupported $Cu^{(0)}$ nanosized particles and structures. Unlike the situation in the recent literature, we will not use the adjective 'metallic' to qualify these nanophases. Attributing the metallic character to a novel copper nanomaterial should necessarily imply an assessment of its electron energy distribution. The chemical bond connecting a limited number of copper atoms clustered in the core of a NP and stabilized by an outer shell composed of other substances, can hardly be regarded as a *metallic* bond.

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Obtaining stable nanomaterials that consist exclusively of chemically pure (elemental) transition metals, without using any stabilizing agent, is an unresolved issue that remains the subject of contrasting opinions [1]. In the case of physical preparation techniques, traces of hydrocarbons deriving from the vacuum systems, gases present in the deposition environment, or other contaminants which come into contact with the NP during real-world applications (e.g. atmospheric oxygen), always give rise to an outer shell – even of submonolayer thickness – which stabilizes the elemental NP core. In solution-based approaches, even when stabilizers are not added intentionally, either the solvent itself or dissolved oxygen can be responsible for interactions with the NP surface, leading to a stabilizing zone that surrounds the particle and has its own composition, which differs from that of the NP core.

In this chapter, when reporting on copper nanomaterials, we will implicitly focus on the nanostructure main part – the core. The existence of a *relatively* thin stabilizing shell (composed of organic stabilizers, copper oxide or hydroxide, chemi- or physisorbed solvent molecules, etc.) surrounding the NP core will be accepted as a natural consequence of both the size and the chemical reactivity of the copper phase.

More complex core-shell structures in which the copper core has been intentionally modified by a *thick* layer of another material (polymer, oxide, other metals, inorganic compounds, etc.) will not be reviewed in this chapter, as they often imply brand-different synthesis approaches. In fact, most of these will form the subjects of other contributions in this textbook series.

As a consequence of all these premises, composite nanostructured materials (including Cu NPs in polymer or silica glass dispersing matrices), Cu_2O and CuO nanoparticles, Cu/Cu oxide core-shell materials, copper-containing compounds and alloys (including magnetic particles), multimetal NPs and supported nanophases (including electrochemically, lithographically or physically deposited nanophases that cannot be easily removed from the substrate without losing their properties), will not be described herein.

The number of studies published on the synthesis and characterization of copper nanomaterials has been growing exponentially in recent years; indeed, a literature search over the period 1991–2007 returned more than 5000 papers and patents [2].

In particular, we based our database search on a combined use of the keyword 'copper' with another one, chosen among the following terms: 'nanoparticle', 'nanocluster', 'nanowire' or 'nanorod'. The results were then analyzed, by publication year and document type. The latter classification was based on two groups – namely patents and academic studies (reviews, commentaries, papers, conferences, etc.) – that we have generically indicated as 'papers'. Histograms relevant to the different classes are reported in Figures 1.1 and 1.2; the former figure shows the distribution of the total number of patents (panel c), papers (panel b), and their sum (panel a), as a function of the publication year. The year-distribution of papers and patents as a function of the single keyword is described in Figure 1.2. A general increase in the publication frequency can be noted in all cases; however,

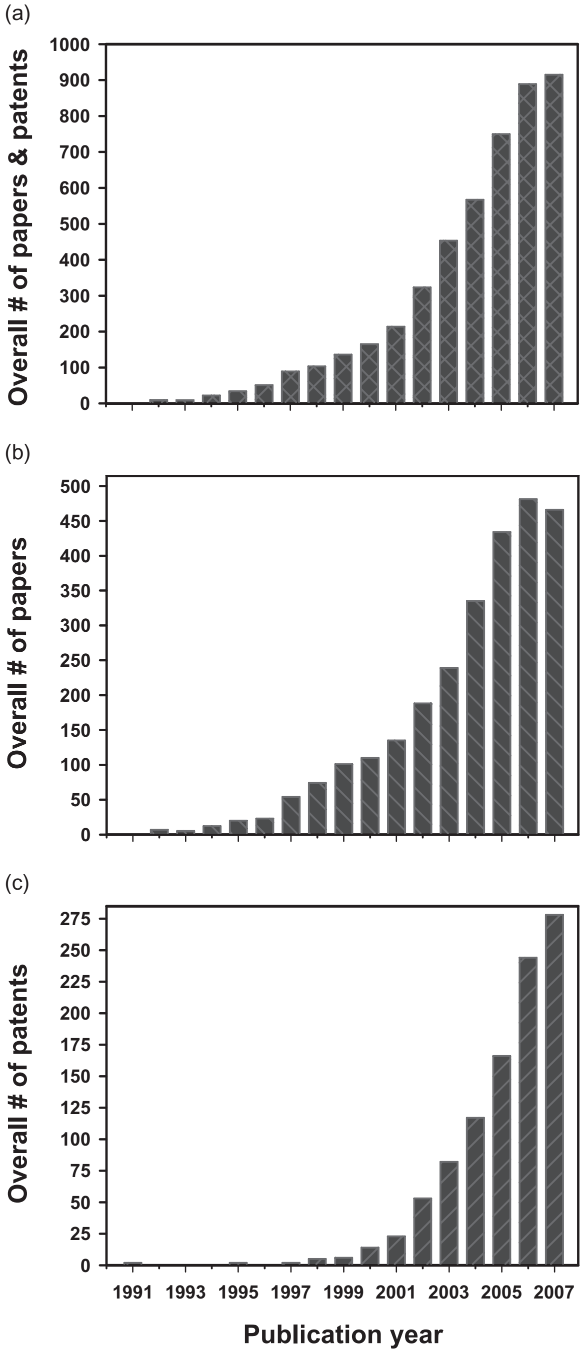

Figure 1.1 Histograms showing the distribution of the total number of patents (c), papers (b), and their sum (a), as a function of the publication year.

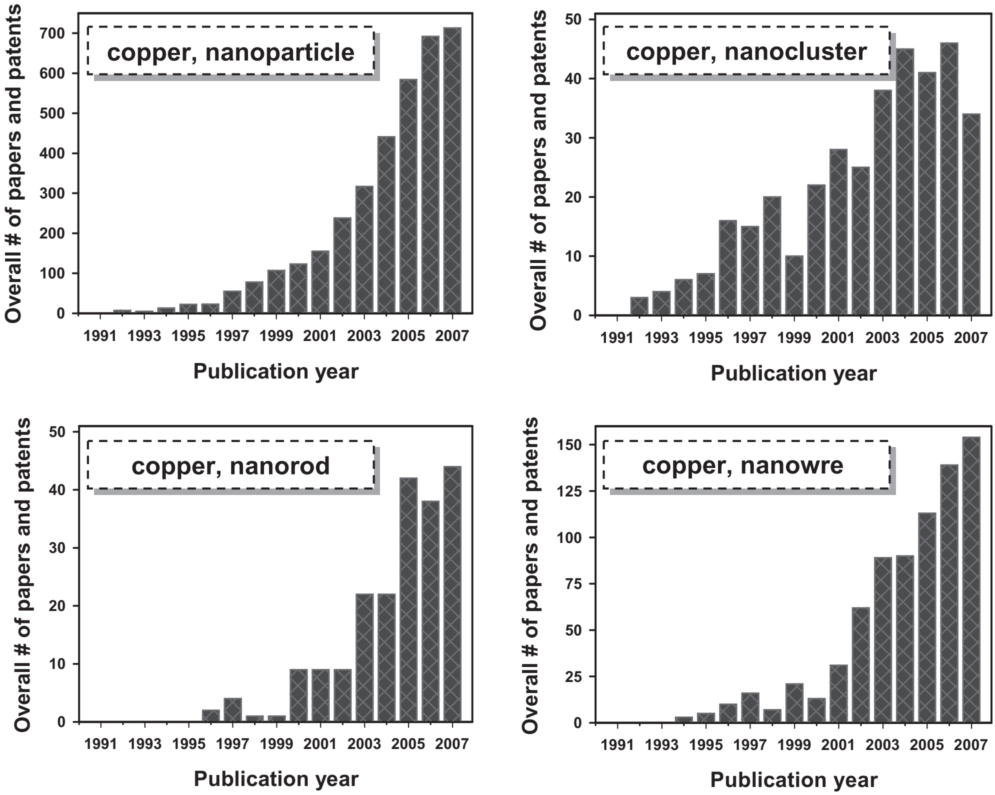

Figure 1.2 Histograms showing the year-distribution of papers and patents as a function of the single keyword.

the number of papers and patents relevant to the keywords 'nanoparticle' and 'nanowire' is markedly higher, as compared with the other two classes; moreover, their trends show a steeper increase in recent years.

Despite the large number of studies and their exponential increase, very few reviews have been issued on the synthesis and characterization of $Cu^{(0)}$ nanostructures, all of them dealing with specific approaches, limited periods or selected morphologies [3–13]. At present, there is therefore the need for a comprehensive review, providing a 'bird's eye view' of all the possible routes for the preparation of nanosized copper materials, and their characterization. Aiming at this purpose, in the present chapter we reported on all the main approaches, and have provided a brief commentary on each of these, following its historical evolution and the key aspects/findings of outstanding studies. As guideline to the classification of the different studies, we chose the type of synthesis approach, while characterization results were cited, in support of the description of specific nanomaterials and/or methods. Consequently, the present chapter is divided into four subsections, respectively devoted to physical, wet-chemical, photochemical and electrochemical methods for the synthesis of copper nanomaterials.

We clearly admit that such a classification is not perfect, and that some interesting studies may have been omitted, due not only to the high number of publications existing but also to the organization chosen for the chapter. Nevertheless, the chapter presents a critical selection of citations taken from the greatest number of studies on Cu NPs referenced to date. It is the authors' intention that the chapter should be considered as a basic aid for the reader who wishes to approach the 'microcosm' of the synthesis and characterization of copper nanomaterials in a concise and schematic manner.

1.2
Physical/Mechanical and Vapor-Phase Approaches

The reader will note that the sections of this chapter which describe chemical (and related) approaches are longer than the present paragraph, dealing with physical/mechanical and vapor-phase approaches. This choice is due basically to a recent remarkable development in the research fields corresponding to chemical approaches, determining a greater literature expansion, as compared to barely physical routes to unsupported $Cu^{(0)}$ NPs. In this section, a technique with great historical and applicative relevance – such as mechanical milling – has been cited concisely, as we believed there to be only a partial overlap between research on metal powders of industrial interest and the main topic of this chapter, namely, the controlled synthesis of Cu NPs with well-defined and uniform properties.

Some infrequent routes to Cu NPs – such as electrical wire explosion, electrospinning and spray pyrolysis – are cited for the sake of completeness, along with more widespread vapor-phase approaches, such as arc discharge, metal vapor and metal–organic vapor condensations.

Due to the aforementioned focus on unsupported $Cu^{(0)}$ NPs, several very important techniques – which lead principally to the deposition of supported or composite nanomaterials (including many plasma approaches, ion-beam sputtering deposition, lithography, etc.) – have not been included in this section.

1.2.1
Mechanical and Mechanochemical Milling

Mechanical techniques, such as ball milling (BM), represent one of the earlier examples of the so-called 'top-down' approaches to nanostructures, involving the controlled erosion of precursors to produce finer structures. Originally, the BM of powders was developed in metallurgy to produce finely dispersed alloys [14, 15], but subsequently it has been used to produce several metastable materials. First examples of the BM preparation of nanocrystalline materials dates back to the early 1990s [16]. The BM of powders is also known as 'mechanical attrition', and can be divided in two categories, as a function of the composition of the starting powder. The milling of elemental powders is indicated as mechanical milling, whereas in the case of powders having different compositions it is indicated as mechanical alloying [17–19]. Although the minimum grain size achieved by mechanical attrition depends on several parameters, the size distribution of ball milled-particles can be quite broad when compared to that of NPs produced by chemical methods [14]. In general, mechanical erosion routes for the preparation of Cu NPs have been frequently outperformed by chemical approaches, due mainly to the less-tight control over NP size, shape and crystallinity.

Several studies were reported during the 1990s on the fundamental aspects of the BM-preparation of Cu NPs [20–26]. More recently, however, an improved version of the method has been proposed, leading to Cu nanograins with a narrower size distribution and good crystallinity [27]. During the 1990s a number of investigations were also conducted on the use of mechanical milling to induce solid-state displacement reactions and to obtain Cu NPs from $Cu^{(II)}$ precursors, such as dichloride [28–30]. Unfortunately, however, this process – which was named *mechanochemical* – showed certain weak points, such as the occurrence of combustion side-reactions, and has not undergone remarkable developments.

1.2.2
Electrical Wire Explosion and Electrospinning Approaches

The technique of electrical wire (EW) explosion has been studied since the 1950s [31–37], and the EW production of Cu nanoclusters and nanopowders has been investigated widely during the past 50 years [32, 33, 38]. In this method, the average particle size can be controlled by the ambient gas pressure, with the particle size usually increasing in line with pressure increases [39, 40]. Other parameters that may influence the final nanopowder include the chemical reactivity of the ambient gas and the initial radius of the wire [41, 42]. Although a number of studies have been reported on the EW production of Cu NPs, it should be noted that the final product of EW synthesis shows very poor stability towards storage or heating in air, due to severe oxidative degradation [43].

Electrospinning (ES) is another high-energy approach to Cu nanostructures, and is based on the application of high voltages. In recent years, this technique has attracted much interest for the preparation of nanofibers and other elongated nanostructures. In the ES process, a high voltage is applied to a polymer solution that is ejected from a conductive capillary. This results in fibers that are collected at a counterelectrode in the form of aligned bundles [44–46]. It is possible to modify the process by adding small-sized Cu NPs to the polymer solution, and to use this mixed precursor to obtain composite metal–polymer nanofibers [47]. Recently, such an approach was applied to the preparation of Cu nanocables capped by poly(vinyl alcohol) from Cu NPs having the same capping agent [48], while a solution of $Cu(NO_3)_2$ and poly(vinyl butyral) was used to produce long, electrospun copper fibers [49].

1.2.3
Spray and Flame-Spray Pyrolysis

Spray pyrolysis (SP) has been used to produce micro-and nanosized particles since the 1990s [50]. In a typical SP synthesis of Cu NPs, an aqueous solution of the correct precursor is atomized and the resultant droplets are transferred by a carrier gas into a tubular furnace (a possible instrumental set-up is shown in Figure 1.3), where the precursor is converted into spherical Cu NPs (see Figure 1.4) [51]. The

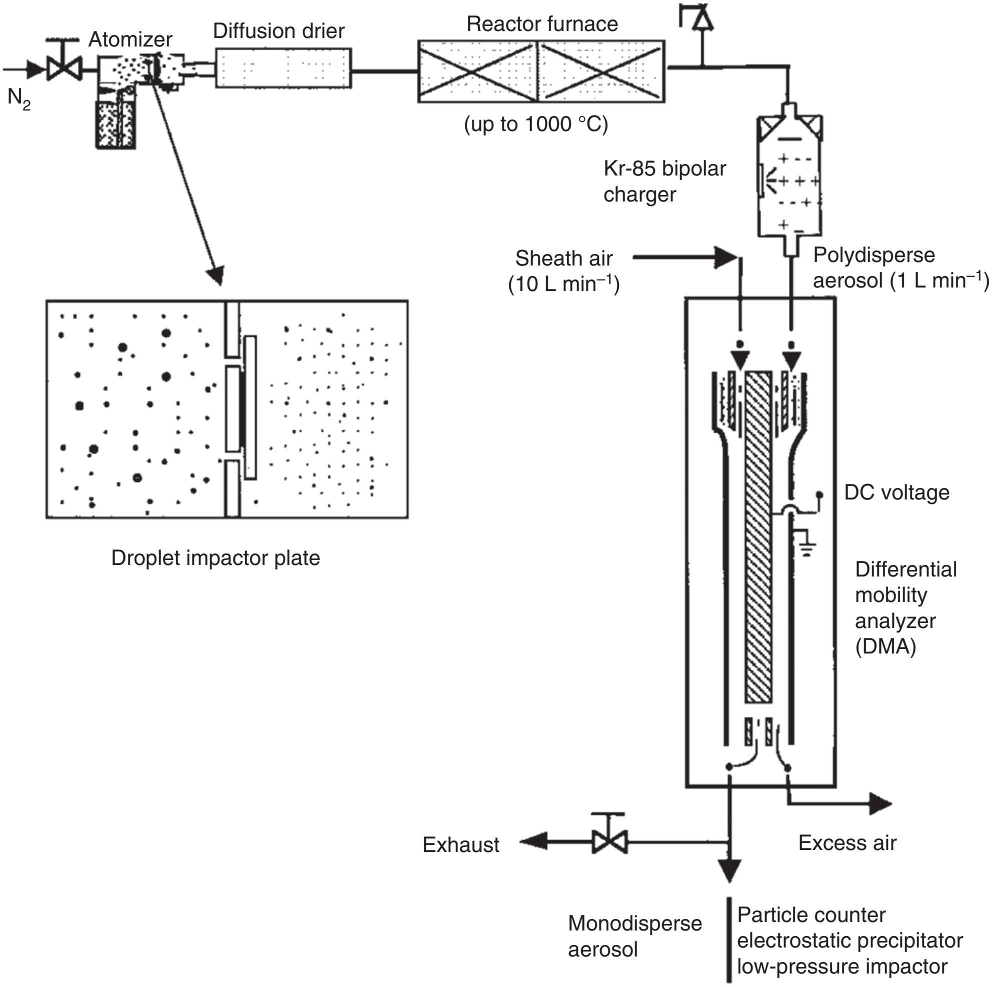

Figure 1.3 Spray pyrolysis system for particle generation and classification. Reprinted with permission from *Advanced Materials* **2002**, *14*(7), 518–21; © 2002 Wiley-VCH Verlag GmbH &Co.

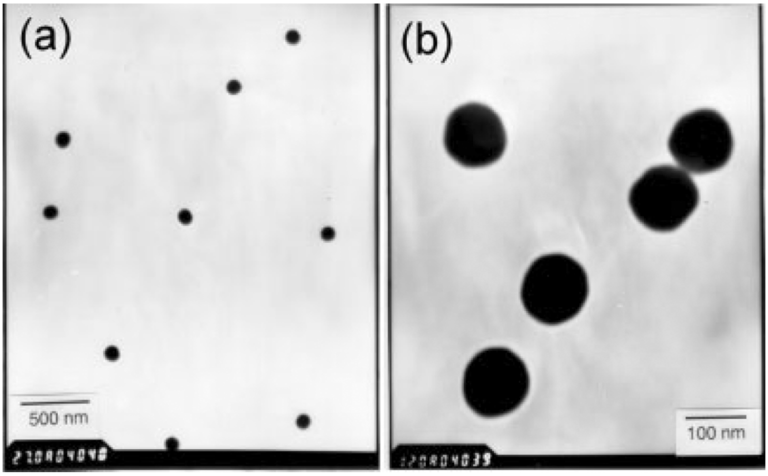

Figure 1.4 TEM images of copper particles produced at 600 °C. (a) original magnification ×27 000; (b) original magnification ×120 000. Reprinted with permission from *Advanced Materials* **2002**, *14*(7), 518–21; © 2002 Wiley-VCH Verlag GmbH &Co.

process is frequently based on the use of relatively high concentrations of H_2, mixed with the carrier gas, to promote reduction of the copper precursor [52, 53], although this procedure may increase potential safety hazards. In an alternative approach, low-molecular-weight alcohols are used as both cosolvent and reducing agent [51]. The key role of alcohols and polyols in the reduction of the copper precursor is discussed in Section 1.3.2. Here, it will simply be noted that the alcohol concentration can be used in SP processes to tune the NP chemical status. Changes in the Cu NP chemical composition induced by adding 10% ethanol to the precursor solution are shown in Figure 1.5 [51].

The application of *flame spray pyrolysis* to NP synthesis generally resulted in the production of metal oxides and salts [54–57]. Recently, Athanassiou *et al.* proposed the use of a flame-SP apparatus which operated in continuous fashion in a nitrogen-filled glovebox to produce carbon-coated Cu NPs with a good size uniformity [58].

1.2.4
Arc-Discharge Approaches

The use of arc discharges under an inert and/or reactive gas, or in liquid phase, implies the generation of a plasma jet inducing the formation of copper atoms and their condensation into particles of different structure and composition [59, 60]. Early investigations into application of the arc-discharge technique to the synthesis of Cu NPs were proposed during the 1990s [61–63], when mixtures of

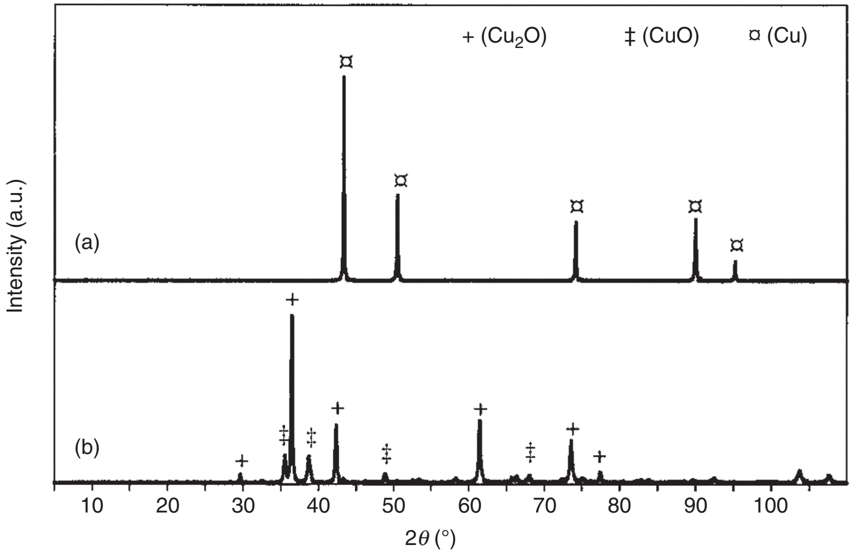

Figure 1.5 X-ray diffraction (XRD) pattern of copper particles prepared at 600 °C from 0.30 mol l^{-1} $Cu(NO_3)_2$ in (a) 10 vol.% ethanol and (b) pure aqueous solutions. Reprinted with permission from *Advanced Materials* **2002**, *14*(7), 518–21; © 2002 Wiley-VCH Verlag GmbH &Co.

an inert gas and hydrogen or methane reactive gases were respectively used to prepare aggregated copper powders [61] or carbon-encapsulated Cu NPs [62]. This is an example of what generally happens in this approach: when preparing Cu nanopowders without additional stabilizing agent, they inevitably tended to aggregate [61] or generate more complex structures [64]. Consequently, in recent years the approach has mainly focused on the encapsulation of Cu nanograins into carbonaceous [65] or polymeric [66, 67] protecting shells. The first class of NPs is basically a development of what was found in 1998 by Jao *et al.* [62], whereas in the second approach arc evaporation/condensation and plasma polymerization techniques were combined in a dual plasma process, leading to polymer-stabilized copper nanoparticles.

More recently, arc-discharge routes have been used in the liquid phase. This method, which is referred to as solid–liquid phase arc discharge (SLPAD), comprises polarizing copper electrodes that are maintained at high voltages and then momentarily short-circuited through an appropriate medium, such as an aqueous electrolyte solution [68], ethylene glycol [69], or an aqueous solution containing antioxidants and surfactants [e.g. ascorbic acid and cetyltrimethylammonium bromide (CTAB)] [70]. The high electrical power generates an arc of high temperatures (10^3–10^4 °C) that induces Cu melting and vaporization such that, close to the electrode surface the liquid is also vaporized and removes the Cu aerosol from the arc zone. The as-formed Cu particles are cooled immediately, preventing their further growth and/or aggregation [69], and then directly dispersed in the liquid phase. By using this method, spindle-like or spherical structures may be obtained in pure solvents such as water [70] or ethylene glycol [69], respectively. The use of additional capping agents was found to increase the stability of spherical NPs in the low-dimensional range [70].

1.2.5
Metal Vapor Condensation

The term inert gas condensation (IGC) indicates a general approach based on the high-energy evaporation of metal atoms and on their subsequent condensation under inert conditions, leading to metal particles [71]. Most frequently, IGC has been performed by thermally evaporating metal atoms, although arc-discharge approaches and sputter-assisted methods [72] can also be considered as IGC processes. The IGC preparation of Cu nanopowders, which dates back to the 1980s, has often suffered from problems associated with unstabilized particles, including polydispersion and air instability, due to oxidation phenomena [73–76]. Many reports published during the 1990s sought to produce nanocrystalline macroscopic materials (by means of compaction or other techniques) [77] or were focused on the study of specific fundamental aspects [78–80]. In 1996, an alternative method was proposed, based on the rapid condensation of metal vapors by contacting them with the vapors of a cryogenic liquid [81, 82]. More recently, the method was modified by collecting metal vapors in a conventional liquid phase (e.g. acetone [83]) or other solvents such as toluene, diglyme and tetrahydrofuran [84].

1.2.6
Metal–Organic Chemical Vapor Condensation

In recent years, organometallic copper species have been employed as precursors for the preparation of Cu NPs via a controlled thermal decomposition process, known as metal–organic chemical vapor deposition (MOCVD). Copper$^{(II)}$-acetylacetonate ($Cu(acac)_2$) and its derivatives have gained wide popularity as precursor compounds for MOCVD routes [85–87], and many of the investigations on this topic have been recently reviewed by the group of E.I. Kauppinen [6]. Basically, the method is based on a controlled decomposition of the organometallic precursor in the vapor phase. In a laminar flow reactor, additional gases were tested as modifiers capable of tuning the nanostructure chemical composition, and elemental, oxide and composite copper NPs have all been obtained using this approach [6]. More recently, ensembles of Cu nanowires were also obtained by thermal decomposition of the same precursor; this had been sealed under vacuum in ampoules and then thermally treated at 300–400 °C [88]. The wire surface was shown to be protected by a thin carbonaceous layer that stabilized the elongated structure. The hexafluoro- derivative of $Cu(acac)_2$ has been also employed in MOCVD routes by the group of Wang [89, 90], who obtained Cu nanowires either by exploiting carbon nanotubes as the templating agent [89] or with controlled crystallization conditions for the growth of Cu structures [90].

Copper (oleate)$_2$ and Cu(II) phthalocyanine compounds were also investigated in similar MOCVD approaches, based respectively on the precursor decomposition in a sealed tube [91–93] or in a tubular reactor [94]. During the period between 2002 and 2004, a quite different approach was used by Bunge *et al.* [95] and Fischer and coworkers [96, 97]. These groups applied a modified version of the procedure developed by Floriani and colleagues [98], and rapidly injected an octylamine solution of a Cu$^{(I)}$-mesityl complex [95] or $Cu(OCH(Me)CH_2NMe_2)_2$ [96, 97] into a hot hexadecylamine solution (at 300 °C). This led to the production of high-quality nanoparticles, namely monodisperse spherical and crystalline Cu$^{(0)}$ NPs (of ca. 10 nm) that were passivated by amino groups.

1.3
Chemical Approaches

Transition-metal nanophases are intrinsically *unstable materials* (the thermodynamic minimum appears always to correspond to the bulk metal) that we can handle, store and use for technological applications exclusively in case the kinetics of their undesired degradation reactions are sufficiently slow. In aiming to slow down the rate of NP side reactions, a large number of investigations have been conducted to determine how the correct *stabilization* of metal NPs can be achieved.

As outlined by R.G. Finke and L.S. Ott in a recent review [1], those species capable of stabilizing a nanosized metal phase can be allocated to three classes, based on their mechanisms of action: (i) *electrostatic*, based on the classical theory of electrostatic colloidal stabilization, as developed by Derjaugin, Landau, Verwey and Overbeek (often referred to by the acronym DLVO); (ii) *steric*; and (iii) *electrosteric*, which is a combination of the electrostatic and steric modes.

Interestingly, the same authors provided a critical viewpoint of how to discriminate among different modes and attribute the role of *stabilizer* to a specific agent. It is a fact that the attribution of a stabilizing effect to a single surfactant/polymer/additive can be misleading: in many systems, there are often multiple possible stabilizers, and frequently the solvent itself, or dissolved counterions, may take part in the NP stabilization. Even the amount of dissolved oxygen can be critical (this is especially true in the case of copper), as the formation of an oxide shell may contribute to either the stabilization or aggregation of NPs.

However, it should also be noted that the choice of a specific stabilizer is presently driving the bibliographic classifications: many papers are specifically titled in terms of the leading stabilizer chosen for the NP preparation, and the number of agents that have been successfully applied to the synthesis of well-dispersed Cu NPs has undergone a vast increase, thus evidencing the need for a comprehensive examination of this field.

These critical issues have concurred to the organization of the following paragraphs, where attention has been paid both to the overall synthetic method (including the reaction medium) and to the stabilizer type. Consequently, the red-ox approaches to Cu nanomaterials (in some cases indicated as wet-chemical processes) have been classified in terms of the stabilizer structure (Sections 1.3.1–1.3.4), the possible use of specific reaction media, such as compressed and supercritical fluids (Section 1.3.5) or ionic liquids (Section 1.3.6), and finally of specific reaction conditions, as in the case of ultrasonic-chemical processes (Section 1.3.7).

1.3.1
Wet-Chemical Routes without Surfactants

Apparently, the simplest solution-based approach to produce copper colloids is the direct reduction of a precursor in an appropriate aqueous solution. Most frequently, an alkaline medium and complexing additives are employed; this is necessary in order to sequester Cu ions and to prevent the undesired formation of insoluble $Cu^{(II)}$ hydroxides, eventually evolving into Cu_2O or CuO NPs. In contrast, the formation of cuprate ions or other soluble $Cu^{(II)}$ complexes makes possible the synthesis of $Cu^{(0)}$ NPs, due to the following reaction scheme [99]:

$$Cu^{2+} + 4OH^- \rightarrow Cu(OH)_4^{2-}$$

$$Cu(OH)_4^{2-} + BH_4^- \rightarrow Cu^{(0)} + BO_2^- + 2OH^- + 3H_2$$

Many studies have used a modified version of this aqueous route to Cu NPs [100–111]; the key aspects of the different approaches are shown schematically in Table 1.1.

During the early stages of research into this approach, submicron powders [101, 109, 112] or irregular smaller powders [103] were obtained; subsequently, the correct choice of the complexing agent and of the operating conditions led to the synthesis of several morphologies, including compact or hollow nanocubes and nanospheres (Figure 1.6) [104, 107], nanorods (Figure 1.7) [110] and ultralong nanowires (Figure 1.8) [105].

During the early 1990s, Tsai and Dye reported on the homogeneous reduction of metals salts with alkalides and electrides in aprotic (nonreducible) solvents, leading to nanoscale metal particles [113, 114]. The approach required some degree of experimental skills and was based on the use of solvated M^- and e^- species, that are among the strongest reducing agents in existence. Subsequently, by using $CuCl_2$ as a precursor, the method was successfully applied to the preparation of Cu NPs.

1.3.2
Wet-Chemical Routes Based on Surfactants and Low-Molecular-Weight Capping Agents

1.3.2.1 Aerosol OT (AOT)-Capped Cu Nanomaterials

The controlled preparation of metal colloids by the chemical reduction of copper salts in the presence of a micellar stabilizing environment was the subject of many

Table 1.1 Overview of different approaches to the synthesis of Cu NPs by means of direct reduction in aqueous solution.

Precursor	Reducing agent	Alkaline pH?	Ligand and/or addition of additives	NP type and mean size	Reference (year)
CuCl	Borohydride	Information not available	Information not available	Information not available	[100] (1996)
CuCl	Ethylene-diamine	Yes	KCl	Spherical, submicron (0.8 ± 0.3 μm)	[101] (1997)
CuCl	NaH_2PO_2 H_2O	Yes	No, but process carried out in autoclave @ 200 °C for 1 day	Micron-sized sponges, nanowalls inside the porous structure	[102] (2006)
$CuBr_2$	Borohydride	n.r.	The solvent itself? (several solvents were tested: water, alcohols, THF, acetonitrile, diethyl-ether, etc.)	Irregular; 10–50 nm	[103] (1999)
$CuCl_2$	Hydrazine	–	No	Low reactant conc. gave compact cubic or spherical NPs; high reactant conc. produced hollow NPs; in both cases, NP size was 100–200 nm	[104] (2005)
$Cu(NO_3)_2$	Hydrazine	Yes	Ethylene-diamine (probably, it also concurred to $Cu^{(II)}$ reduction)	Ultralong nanowires (diameter 100–200 nm) or nanodisks	[105] (2005)
$CuSO_4$	Borohydride	Yes	Trisodium citrate	Spherical; 10–30 nm	[106] (2007)
$CuSO_4$	Borohydride	Yes	EDTA	Elliptical; 20 nm	[99] (2005)
$CuSO_4$	Formaldehyde	Yes	Sodium tartrate; silica or polymer nanospheres were used as template	Hollow spherical aggregates; 200–300 nm	[107] (2005)
$CuSO_4$	Borohydride	Yes	I^- or SCN^-	Spherical; 10 nm	[108] (2002)
$CuSO_4$	Borohydride	No, but it increased during the process	No	Submicron powders; 200 nm	[109] (1999)

Table 1.1 *Continued*

Precursor	Reducing agent	Alkaline pH?	Ligand and/or addition of additives	NP type and mean size	Reference (year)
$CuSO_4$	Glucose	Yes	Glucose itself (optimization of its conc. proved to show an effect on the Cu NP morphology)	Spherical (~5 or 20 nm), rod-like (diameter ~50 nm, aspect ratio ~2.5)	[110] (2006)
$CuSO_4$	Hydrazine	n.r.	Hexanol, dimethyl oxalate. First step was the precipitation of spherical $Cu^{(II)}$-oxalate aggregates, acting as a template	Flower-like microcrystals	[111] (2006)

n.r. = not relevant for comparison.

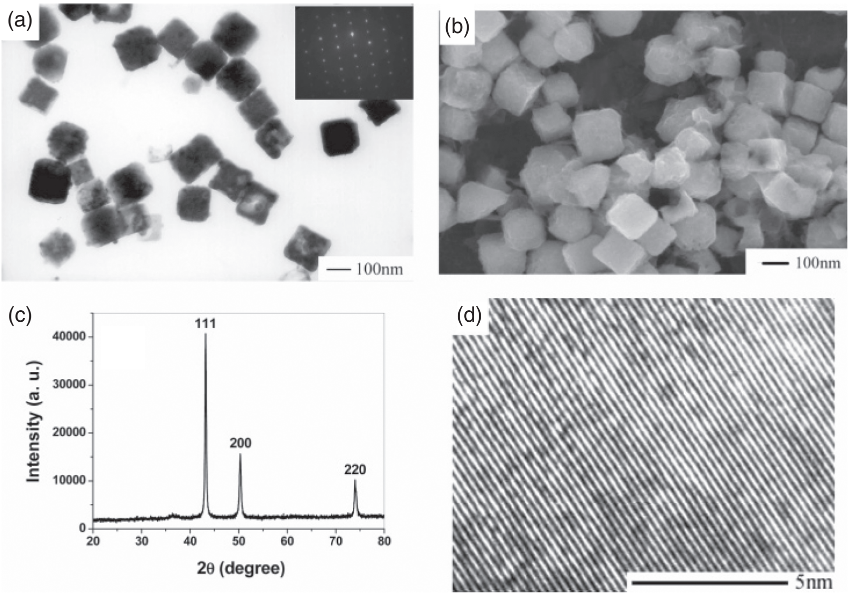

Figure 1.6 (a) TEM and (b) SEM images of cubic copper particles. The inset in (a) shows the selected-area electron diffraction (SAED) pattern obtained by focusing the electron beam on a cubic copper particle; (c) An XRD pattern of copper particles; (d) a high-resolution TEM image of one part of a cubic particle, showing its crystal structure. Reprinted with permission from *Journal of Physical Chemistry B* **2005**, *109*, 15803–7; © 2005 American Chemical Society.

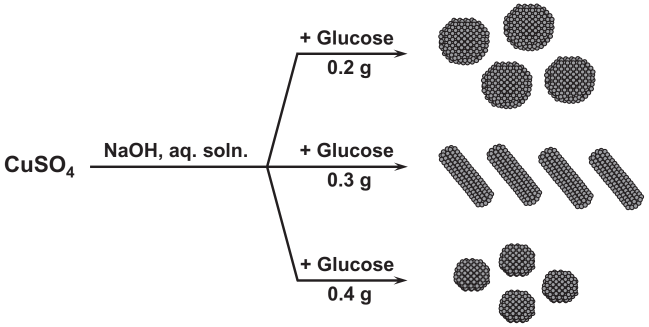

Figure 1.7 Schematic representation of the synthetic procedure proposed by T. Pal and colleagues [110] for the preparation of glucose-capped spherical and rod-shaped copper nanoparticles.

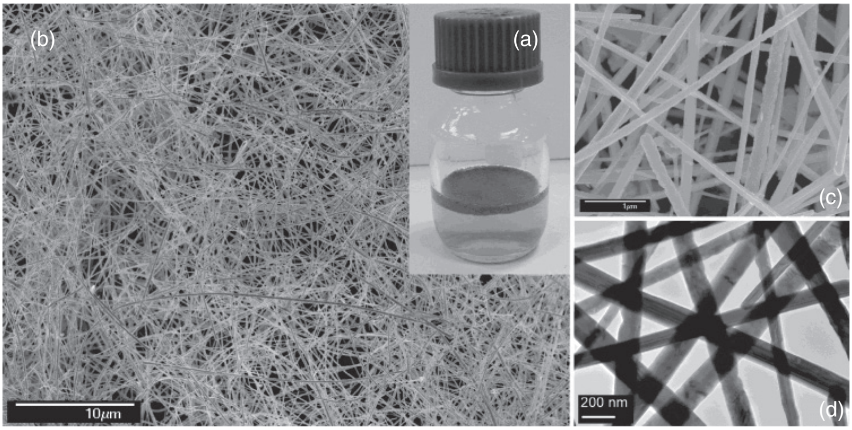

Figure 1.8 (a) As-prepared copper nanowires in mother liquor; (b, c) Field emission SEM images of general and detailed views of copper nanowires; (d) TEM image of copper nanowires. Reprinted with permission from *Langmuir* **2005**, *21*, 3746–8; © 2005 American Chemical Society.

studies during the 1990s, and has continued to develop tremendously during the past decade. This approach, which is often referred to as ‘soft-wet-chemical’, ‘soft colloidal template’ or ‘microemulsion-based’, is based on the use of reducing agents such as hydrazine and sodium borohydride, and has been successfully applied to the preparation of NPs composed not only of transition metals but also other compounds, salts and multimetal particles.

In this respect, many single-chained surfactants have been investigated, including sodium alkyl- or aryl-sulfates [sodium dodecyl sulfate (SDS), sodium benzyl sulfate (SBS) and sodium dodecylbenzene sulfonate (SDBS), quaternary ammonium halides (CTAB, cetyltrimethylammonium chloride (CTAC)]. However, the first and most frequent route to surfactant-stabilized copper nanoparticles is based on use of the di-(2-ethylhexyl)-sulfosuccinate anion, usually indicated by the acronym AOT (Figure 1.9) (for reviews dealing with NP soft-chemical syntheses using AOT, see Ref [7, 11–13, 115–122]).

AOT is a key species for the realization of thermodynamically stable reverse micelles in a ternary water/organic solvent/AOT salt system. Water-in-oil (w/o) microemulsions with a well-defined order and shape can be easily generated by correct selection of the operating conditions (emulsion composition, AOT counterion type, cosurfactant, temperature, pressure, etc.). Since 1991 [123–130], the outstanding studies published by the group of M.P. Pileni have shed light on the potentialities of this system for the controlled preparation of Cu NPs. As several interesting reviews have already been published by the same group on this topic [7, 11–13, 121, 122], we will limit our description here to a very brief survey of the existing literature.

In the case of surfactants consisting of a large polar head and a small lipophilic chain, a normal micelle is formed, in which the chains form the inner core and the polar groups are localized at the outer surface. In contrast, surfactant molecules with small polar moieties and bulky hydrocarbon chains tend to generate *reverse micelles* (see Ref. [121] and references therein), in which the mutual position of polar and nonpolar moieties is exchanged, as compared to the ‘normal’ case. As water becomes entrapped in the core of reverse micelles, there is a dynamic exchange of species within the micelle, and this is where the chemical reduction of the copper precursor occurs. Under selected experimental conditions, an increase in the water : surfactant molar ratio in the emulsion implies a proportional size increase of the template structure. In general, this provides a simple means of controlling the size of spherical Cu NPs generated in the polar core of the nanoreactors. Transmission electron microscopy (TEM) images of colloidal NPs obtained by varying the water content in a $Cu(AOT)_2$/water/isooctane system are shown in Figure 1.10 (top row), together with a sketch of the w/o droplet structure. Of note, such clear size control has been demonstrated in the case of relatively small w/o structures. Other self-assembled structures also become possible, as a

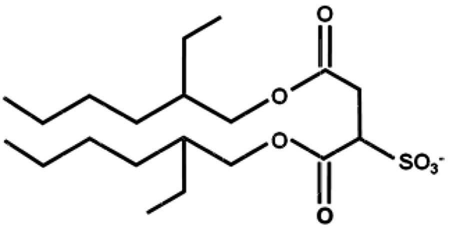

Figure 1.9 Chemical structure of the AOT anion. The branched chains afford for a surfactant shape frequently indicated as a ‘champagne-cork’, due to the bulky lipophilic moieties and a relatively small polar head.

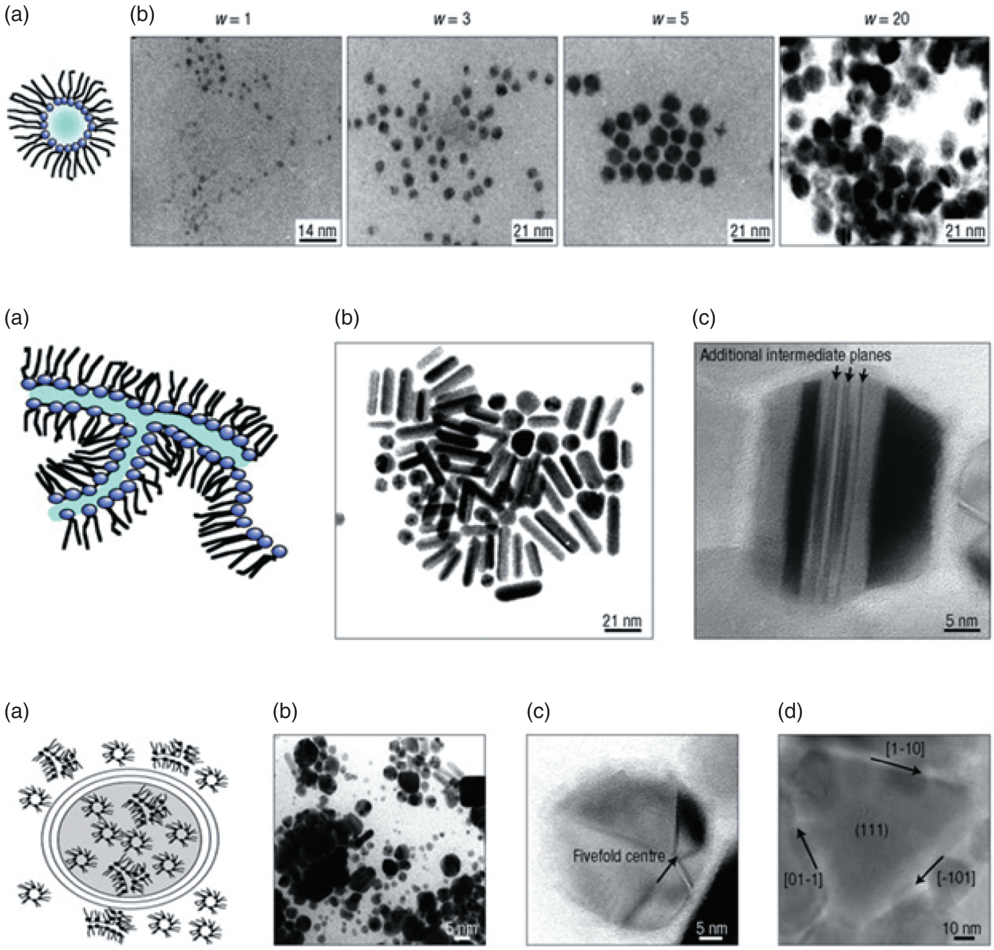

Figure 1.10 Different shapes of copper nanocrystals obtained in colloidal self-assemblies of a surfactant-H_2O-isooctane system. The surfactant, S, employed is either Na(AOT) or $Cu(AOT)_2$. The water amount $w = [H_2O]/[S]$ is related to the droplet radius by $R\ (nm) = 0.15 \times w$. Top row: $[AOT] = 0.1\,M$; $[Cu(AOT)_2] = 10^{-2}\,M$; $[N_2H_4] = 2 \times 10^{-2}\,M$. (a) Reverse micelles; (b) Control of nanocrystal size by means of the control of the size of water-in-oil droplets, w. Middle row: $[Cu(AOT)_2] = 5 \times 10^{-2}\,M$, $[N_2H_4] = 1.5 \times 10^{-1}\,M$, $w = 10$. (a) Interconnected cylinders; (b) formation of spherical and cylindrical nanocrystals; (c) cylindrical particle made of a set of deformed f.c.c. tetrahedra bounded by (111) faces parallel to the fivefold axis with additional lanes. Bottom row: $[Cu(AOT)_2] = 5 \times 10^{-2}\,M$, $[N_2H_4] = 1.5 \times 10^{-1}\,M$, $w = 20$. (a) Supra-aggregates; (b) nanocrystals; (c) particle composed of five deformed f.c.c. tetrahedra bounded by (111) planes; (d) large, flat nanocrystals [111]-oriented and limited by (111) faces at the top, bottom and edges. Reprinted with permission from Macmillan Publisher Ltd: *Nature Materials*, Pileni, M.P., **2003**, *2*, 145; © 2003.

function of the region of the phase-diagram in which the chemical reduction is operated. Insights into the phase composition of several surfactant/water/oil systems have already been reported [131–137], and a direct relationship between template morphology and the synthesis of Cu NPs has been demonstrated [11, 138–140]. For example, in the case of large amounts of both water and organic solvent, water channels/cylinders are generated in the system, thus allowing the growth of cylindrical Cu nanocrystals (Figure 1.10; middle row). Under other experimental conditions planar or onion-like lamellar phases are also possible, and their existence implies other Cu NP morphologies (see Figure 1.10; bottom row).

Whilst the micellar shape cannot afford for a tight size-control over NP shapes which differ from spherical, it has been shown that the presence of different salt ions in the aforementioned water cylinders may provide an independent and useful tool to prepare cubic NPs (in the presence of Br^- ions), elongated particles (in the presence of HSO_3^- ions), Cu nanorods (in the presence of relatively high Cl^- concentrations), or more elongated structures, namely Cu nanowires (in the presence of relatively low Cl^- concentrations, e.g. 1 m*M*) (see Figure 1.11) [141–143].

The use of alternative anionic surfactants such as SDS [144], or the use of AOT mixed with cationic surfactants [145] in more complex w/o microemulsions, has also been explored. Similar to the case of other metals, for the w/AOT/oil soft-synthesis of Cu NPs, a number of reducing agents has been investigated: hydrazine and $NaBH_4$ are definitively the most frequently employed, although alternative chemicals, including natural molecules such as quercetin [146] have also been proposed. More recently, the group of Pileni has shown that a large excess of hydrazine, when employed as reducing agent, can give access to other anisotropic morphologies such as Cu nanotriangles [147] and nanodisks [148] (Figure 1.12).

As interestingly outlined by Pileni [121], the changes in the Cu NPs shape are attributed to differences in the growth rate of crystallographic faces, and

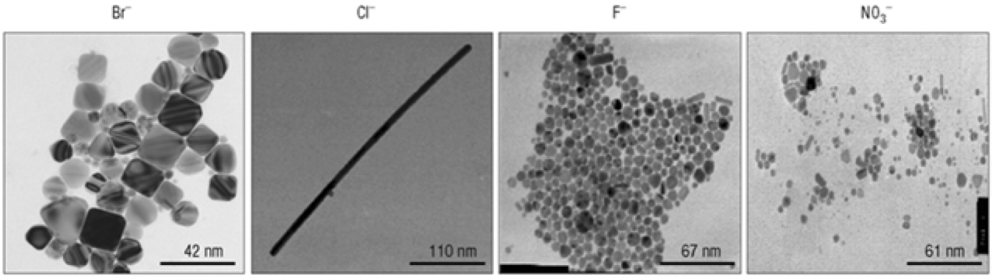

Figure 1.11 Different shapes of copper nanocrystals obtained in interconnected cylinders in the presence of various salt ions having the same concentration. 5×10^{-2} *M* $Cu(AOT)_2$ was dissolved in isooctane in the presence of various salts. Hydrazine was added to obtain $w = 10$ and a 10^{-1} *M* overall concentration $[N_2H_4]$, [NaCl] = [NaBr] = [NaF] = $[NaNO_3] = 10^{-3}$ *M*. Reprinted with permission from Macmillan Publisher Ltd. *Nature Materials*, Pileni, M.P., **2003**, *2*, 145; © 2003.

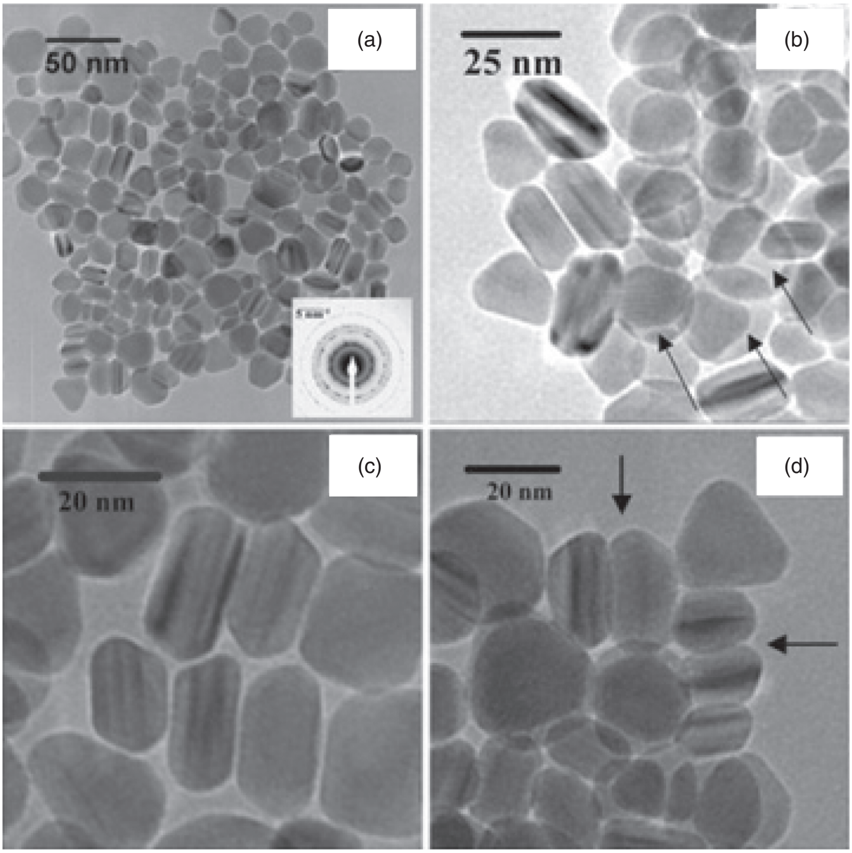

Figure 1.12 TEM images of copper nanocrystals. (a) Copper nanocrystals – the inset shows the SAED pattern of a collection of copper nanocrystals; (b) Thin nanocrystals; (c) Stacked elongated nanocrystals; (d) Overlapped nanocrystals. Reprinted with permission from *Advanced Functional Materials* **2005**, *15*, 1277–84; © 2005 Wiley-VCH Verlag GmbH &Co.

this is correlated to the selective adsorption of species/additives during crystal growth.

Other studies conducted by the group of C.R. Roberts have provided details about particle growth kinetics [149, 150]. Basically, as the ratio of the absorbance detected at about 560 nm (corresponding to the peak maximum) and 500 nm (off-peak) is correlated directly to the mean size of the Cu NPs core, these authors performed time-resolved *in situ* studies and followed the evolution of spherical Cu NPs, in turn proposing a theoretical model able to predict the NP size.

It is a fact that the chemical and physical properties of NPs can be tailored by controlling their size and/or their shape (see Ref. [151] and references therein; see also Refs [152, 153]). In Ref. [154], copper nanocrystals of different shapes were shown to give rise to different UV-visible absorption features. In particular, the well-known plasmon resonance peak which falls at about 560 nm is attributed to spherical and cubo-octahedral NPs, whereas the peak falling at 650 nm can be shown to correlate to nanosized copper disks. Both, simulated and experimental UV-visible spectra obtained with Cu nanodisks prepared in reverse micelles are shown in Figure 1.13 [154, 155].

1.3.2.2 Alkyl-Phosphate-Capped Cu NPs

Bis(ethylhexyl)hydrogen phosphate (HDEHP) [156] and other phosphate derivatives, such as dialkyl-dithio-phosphates (DDP) [157, 158], have been recently proposed as capping agents, as alternatives to AOT, for the w/o synthesis of spherical Cu NPs. The chemical structure and ability to form micellar structures of these surfactants strongly resemble those of AOT; both HDEHP and DDP are characterized by a 'champagne-cork' aspect, and form reverse micelles in w/o mixed solvents. Consequently, Cu NPs could be easily generated using the approach already described for AOT. The NPs showed good film-forming properties, while the presence of DDP stabilizers afforded useful antiwear properties when used as additives in liquid paraffin [157, 158].

1.3.2.3 Alkyl-Sulfate-Capped Cu NPs

Another microemulsion route to Cu NPs is based on the use of sodium alkyl- or aryl-sulfates. Two anionic surfactants have been frequently employed, namely SDS [159–161] and SDBS [162], both of which generate micellar aggregates that are similar to those described in the above sections. For example, in 1999 Qiu *et al*. showed that the size of w/o droplets (in a microemulsion composed of SDS, isopentanol, cyclohexane and water) depended linearly on the water/SDS molar ratio, and that this parameter could be used to tune the size of spherical Cu NPs [159].

More recently, SDS has been used mixed with polysorbates (Tweens) in order to exploit the synergetic stabilizing effects [161] whilst, in a simplified approach, Lu and coworkers obtained Cu nanocubes (Figure 1.14) through the hydrazine-reduction of $CuCl_2$ in refluxing aqueous solutions containing millimolar concentrations of SDBS [162]. The latter route could also be successfully applied to other metals and bimetallic particles.

1.3.2.4 Alkyl-Thiol-Capped Cu NPs

The synthesis of thiol-capped nanocopper is basically a further development/modification of the Brust approach, that was originally applied to gold NPs [163]. In a typical reaction, a $Cu^{(II)}$ salt is dissolved in a polar solvent (usually water [164–166], although methanol has been also used [167]), and then mixed/shaken with a solution of a quaternary ammonium salt ['quat', frequently, a cetyltrimethylammonium (CTA) or tetra-octylammonium (TOA) bromide] dissolved in an apolar solvent such as toluene. A thiol capping agent is subsequently added, and in the last step $NaBH_4$ or an equivalent reducing agent is added dropwise. Due to ligand

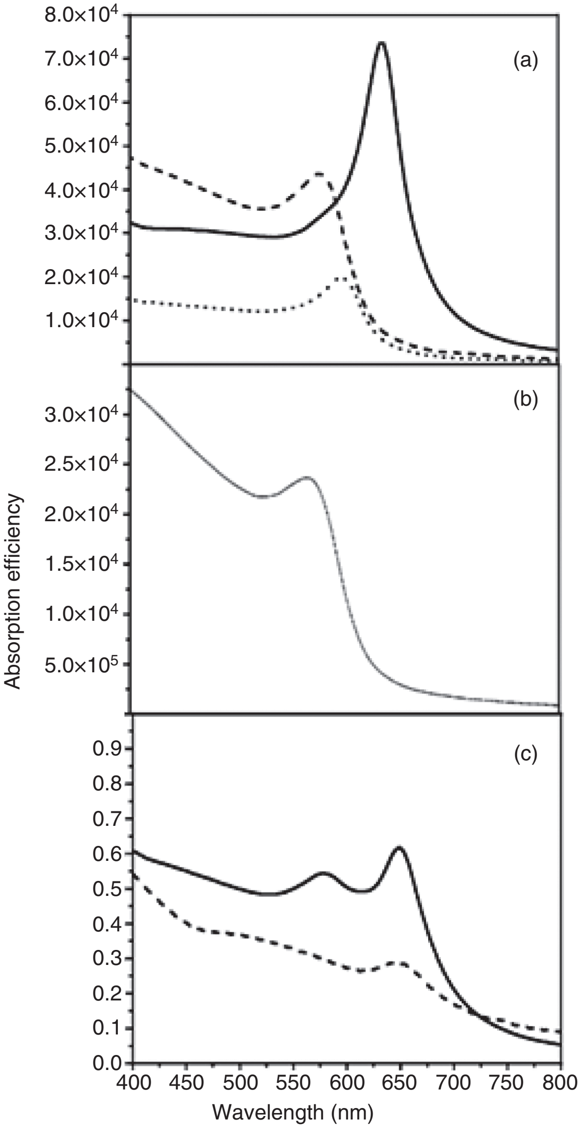

Figure 1.13 (a) Simulated absorption spectrum of copper particles having different shapes: nanodisks (size = 23 nm, aspect ratio = 1.8, truncature = 0), solid line; elongated particles (length = 22, width = 13, aspect ratio = 1.8), dotted line; cubo-octahedra (19 nm), dashed line; (b) Simulated absorption spectrum of 20 nm spherical copper particles; (c) Comparison between the experimental (dashed line) and simulated spectra (solid line). Reprinted with permission from *Journal of Physical Chemistry B* **2006**, *110*, 7208–12; © 2006 American Chemical Society.

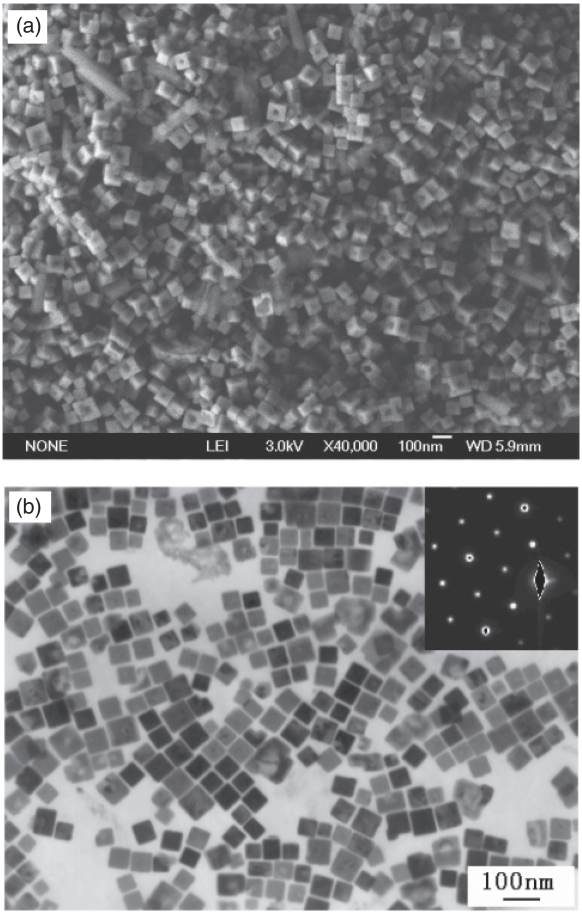

Figure 1.14 (a) SEM and (b) TEM images of copper nanocubes prepared under the final concentration $C_{CuCl2} = 0.1\,mM$ and $C_{N2H4} = 3\,mM$ and refluxed for 20 min at 100 °C in the presence of 1 m*M* SDBS. The inset in (b) shows the SAED pattern obtained by directing the electron beam parallel to the <111> direction. Reprinted with permission from *Langmuir* **2006**, *22*, 5900–3; © 2006 American Chemical Society.

exchange, the quat species are substituted by the thiol. Finally, alkyl-thiolate-Cu NPs can be collected/extracted in an appropriate organic phase such as toluene or benzene.

The effects of ligand structure on the stability of as-synthesized Cu NPs were assessed in several studies [164, 168–170]. Based on the appreciable stabilization provided by the thiol moieties, these core-shell NPs were subjected to several interesting investigations. For example, in differential pulse voltammetry experiments, Chen and Sommers observed that the as-produced Cu NPs showed quantized charging features [165]. Neckers and collaborators prepared Cu NPs capped by modified thiols bearing acrylic ending groups, allowing the copolymerization of Cu NPs and acrylic monomers [167]. Finally, Dong *et al.* were able to prepare highly ordered Cu NP superlattices, by a controlled thermal annealing of octanethiolate-capped Cu NPs in molten TOA bromide [171].

1.3.2.5 **Cu NPs Capped by Quaternary Ammonium Surfactants**

Many examples have recently been reported of quaternary ammonium surfactants being employed directly as Cu NP capping agents, without making use of any ligand-exchange protocols. In two reports, TOA bromide or ethyl-hexadecyl-dimethyl-ammonium bromide were used to synthesize stabilized Cu NPs subjected to *in situ* spectroscopic investigations, such as XANES (X-ray absorption near-edge structure) [172] or EPR (electron paramagnetic resonance) [173]. The former study dates back to 1998, and provided interesting information about the existence of intermediate states during the formation of colloidal copper in toluene [172], whereas the latter was proposed as a general approach to the direct study of Cu NP oxidation kinetics [173]. Other papers have specifically investigated the potentialities of CTAB in the aqueous synthesis of Cu nanomaterials. In 2003, Cao *et al.* showed that it was possible to prepare nanotubes or nanorods composed of $Cu^{(0)}$ or its oxides, as a function of the experimental conditions [174]. The procedure was carried out in the presence of relatively high CTAB concentrations, but was quite simple as it could be considered a modified version of the simple reduction of an alkaline $Cu^{(II)}$ solution by means of hydrazine. In Ref. [174] evidence was provided that, upon increasing the $Cu^{(II)}$ initial concentration, the morphology of Cu nanostructures changed from nanotube to nanorod (see Figure 1.15 for examples of rod-like nanostructures). The authors hypothesized that electrostatic interactions induced the formation of ion pairs between CTA^+ and $Cu(OH)_4^{2-}$, and that modifying their relative abundances resulted in a change in the micellar aggregate shape.

By using the same chemical species, but different experimental conditions, Wu and Chen where able to prepare highly concentrated solutions of CTAB-capped Cu NPs (up to 0.2 *M*) at room temperature [175]. A slightly different approach was followed by Athawle *et al.*, who employed isopropanol as both reducing agent and organic additive for the preparation of Cu NPs [176, 177]. Kumar and collaborators used a sulfobetaine stabilizer for the alkyl-borohydride conversion of $Cu^{(II)}$ ions into spherical Cu NPs; the use of the zwitterion aimed at improving the compatibility of Cu NPs with polar solvents [178]. These authors investigated two possible approaches, namely a batch and a microfluidic reactor process, and used reaction calorimetric investigations to study the intermediates involved in the NP synthesis.

1.3.2.6 **Cu NPs Capped by Nonionic Surfactants or Stabilizers**

During the late 1990s, the synthesis was reported of Cu NPs stabilized by nonionic commercially available surfactants such as Triton X-100 [179] and Genamin TO20 [180]. These surfactants were employed to generate reverse micelles and spherulite aggregates, respectively (Figure 1.16). The reduction of $Cu^{(II)}$ precursors encapsulated into spherulites was performed by conventional hydrazine treatment such

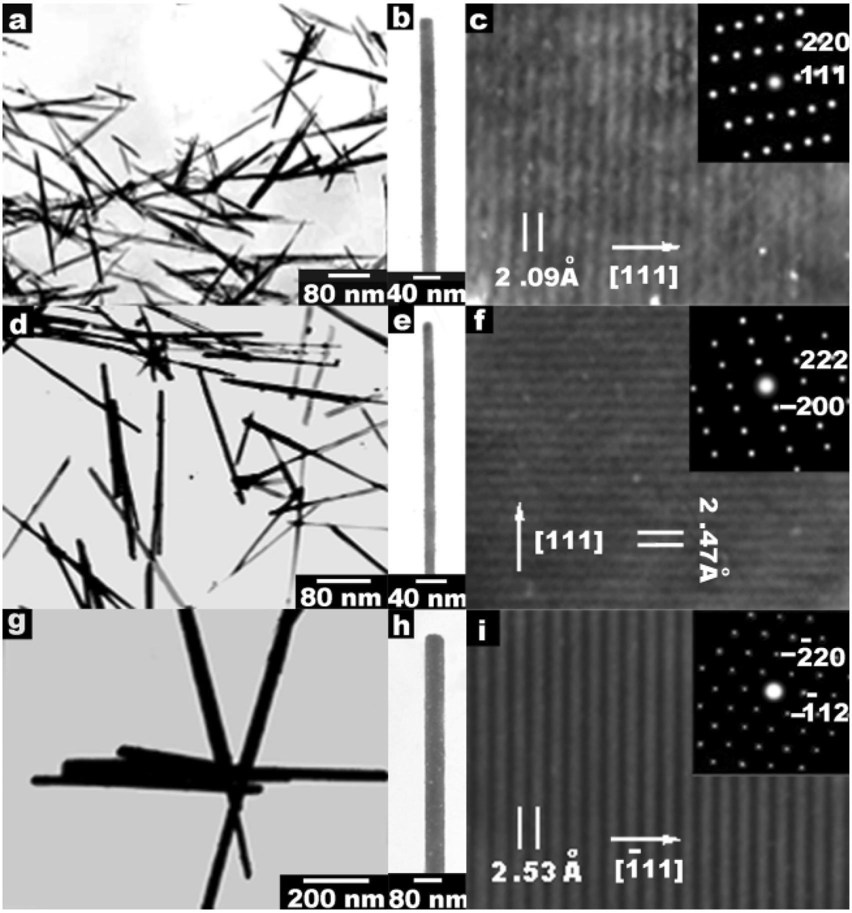

Figure 1.15 TEM images of Cu (a), Cu_2O (d) and CuO (g) nanorods. Single nanorod images of (b) Cu, Cu_2O (e) and CuO (h). High-resolution TEM micrographs of Cu (c), Cu_2O (f) and CuO (i) nanorods. The insets are SAED images of Cu, Cu_2O and CuO nanorods, respectively. Reproduced with kind permission from © Royal Society of Chemistry; DOI: 10.1039/b304505f.

that Cu NPs could be obtained. A phase diagram showing the typical experimental conditions used to prepare spherulites is shown in Figure 1.17. Interestingly, in the case of Genamin TO20, small Cu NPs were aggregated in spherical macroclusters which resembled the shape and size of the spherulite templates (Figure 1.18).

1.3.2.7 **Cu NPs Capped by Cysteine, Oleic Acid and Other Small Molecules with Biological Relevance**

Small biomolecules such as cysteine [181, 182], oleic acid [183–186] and/or oleamine [187, 188] have been intensely investigated during the past two years as

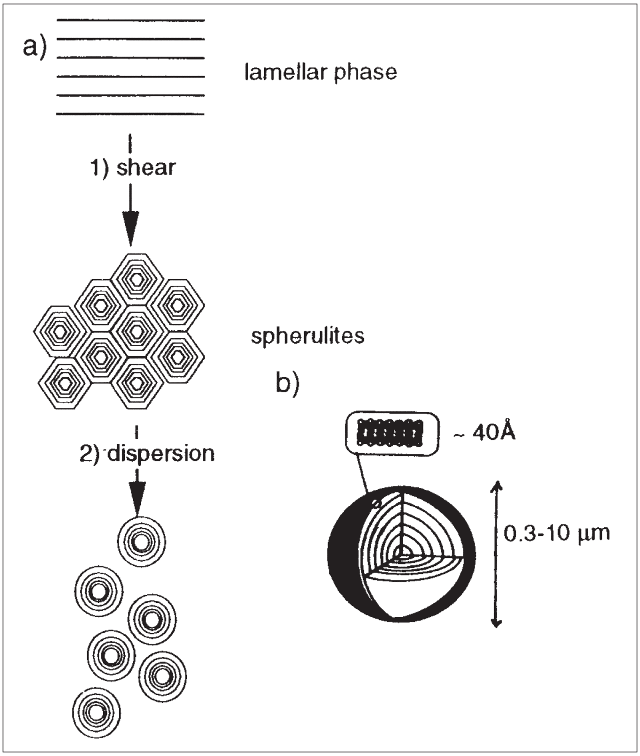

Figure 1.16 Stages in the preparation of a dispersion of spherulites (a) and their structure (b). (a) Route (1): the lamellar phase, under a controlled shear, organizes in a close-packed structure of multilamellar vesicles called spherulites; route (2): spherulites can be dispersed in an excess quantity of solvent; (b) Spherulites are composed of a regular stack of membranes separated by water layers. Reprinted with permission from *Langmuir* **1999**, *15*, 3738–47; © 1999 American Chemical Society.

innovative stabilizers for Cu NPs. Although at present they have been exclusively applied as catalysts [181, 182], amino acid-capped Cu NPs hold great promise in other fields, including the biofunctionalization of metal nanomaterials for biomedical applications, where they combine the properties of a biocompatible shell with those of a copper core capable of releasing antimicrobial ions under tightly controlled kinetics [189]. Using oleic acid as stabilizer and a mild multistep reduction based on glucose and ascorbic acid, Yang *et al.* obtained nanocrystalline copper with an hydrophobic shell, by means of the so-called AOIRT (Aqueous Organic Interface Reaction Technique) method [183–185]. In 2007, the group of Zhong reported a temperature-controlled route to Cu nanocrystals capped by oleic acid and oleamine [187]. The NP size was shown to depend linearly on the reaction temperature, in the 150–190 °C range, while higher values were found to induce the simultaneous formation of several shapes (cubic, tetrahedral, elongated, etc.). In the same year, Liu *et al.* applied a similar approach, in the presence of oleamine

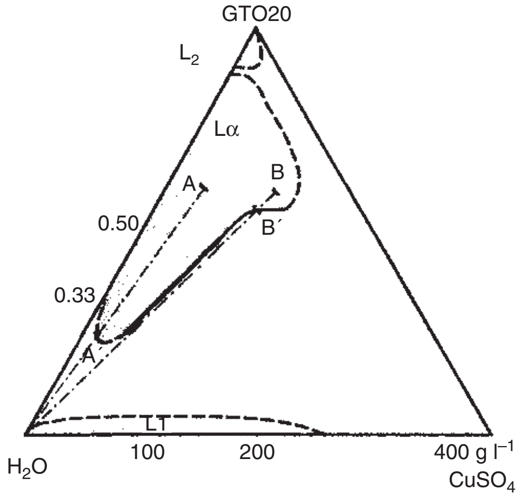

Figure 1.17 Experimental phase diagram of the Genamin TO20/H_2O/$CuSO_4$ system: Lα, lamellar; L_1, micellar; L_2, crystalline. The dashed lines are rough boundaries. Reprinted with permission from *Langmuir* **1999**, *15*, 3738–47; © 1999 American Chemical Society.

[188], to the preparation of Cu, Cu_2O and CuO NPs, while Su *et al*. obtained Cu cubic nanocages in the presence of sodium oleate [186]. Of note, in the latter case the formation of cubic-shaped and empty nanocages was shown to correlate with the structure of the Cu_2O intermediate particles.

1.3.3
Wet-Chemical Routes Based on Polymer and Dendrimer Capping Agents

Polymers represent one of the most frequently studied examples of NPs stabilizer showing steric effects. Physical hindrance of the space around the nanoclusters can prevent/minimize the direct contact between the NP metal cores, and thus afford an increased morphological stability. Polymer-capped Cu colloids have been investigated since the 1980s [190–193]; nano-Cu/polymer interface phenomena can be interpreted as cooperative noncovalent interactions of polymeric chains with surface metal atoms [193]. Moreover, the polymer action is due, at least partially, to the complexation of nanocluster surface atoms; polymer functional groups may in fact generate stronger interactions, leading to highly stabilized copper–polymer complexes.

The approaches to polymer-stabilized copper nanomaterials can be divided into three main classes: (i) the so-called ‘polyol process’; (ii) soft-template processes in which the polymer is employed (either as such or in combination with other capping agents), aiming exclusively at stabilization of the Cu phases; and (iii) dendrimer-encapsulation.

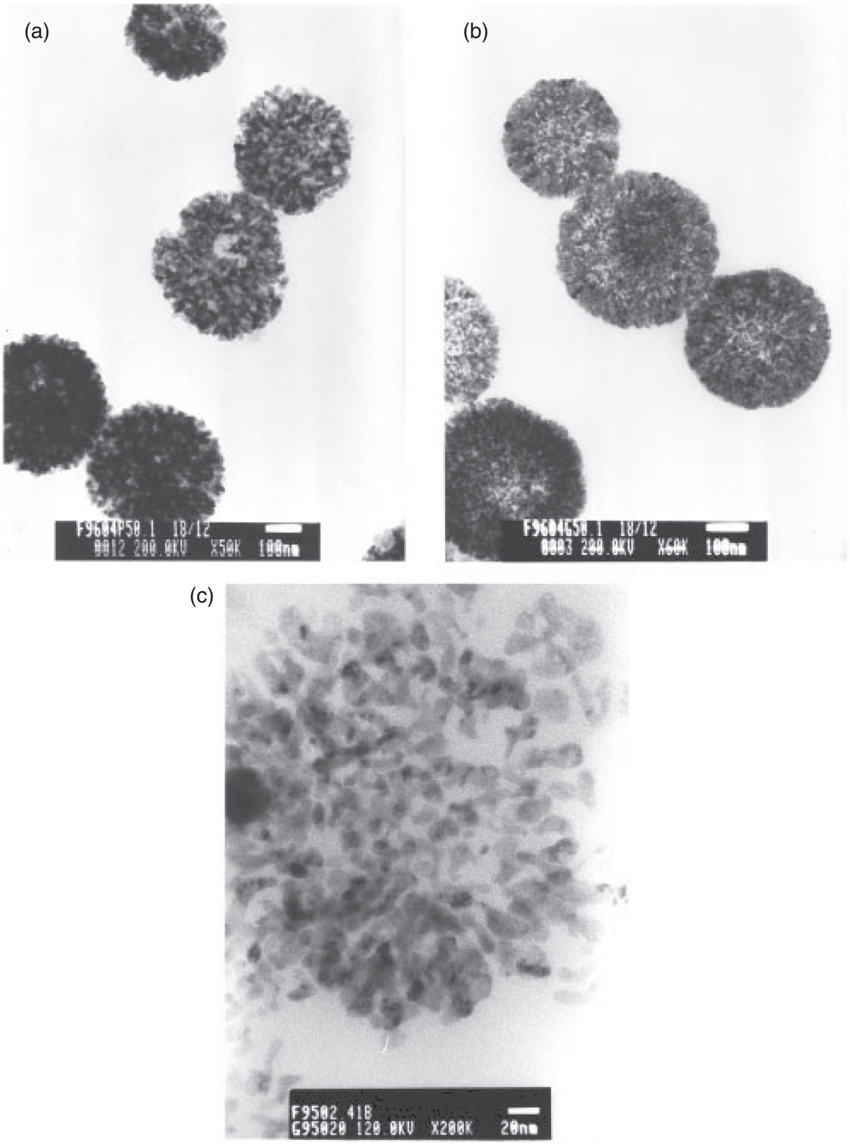

Figure 1.18 TEM images of spherulites after reduction of the encapsulated copper sulfate: (a) $C = 144\,\text{g}\,\text{l}^{-1}$, φ (volumic fraction in surfactant) = 0.54, manual shear; (b) $C = 85\,\text{g}\,\text{l}^{-1}$, $\varphi = 0.54$, shear rate = $107\,\text{s}^{-1}$; (c) Magnification of a single spherulite. Reprinted with permission from *Langmuir* **1999**, *15*, 3738–47; © 1999 American Chemical Society.

1.3.3.1 The Polyol Process

The polyol route to Cu NPs consists of the reduction of an appropriate precursor (copper salts, oxide, hydroxide, etc.) in a liquid alcohol medium, at relatively moderate temperatures. The solvent is typically glycerol or a glycol derivative (e.g. ethylene, diethylene), and has the dual role of a reducing and dispersing agent; to some extent it may also be useful as capping agent [194, 195], although more frequently additional stabilizers are employed [196–200]. Several parameters can be separately adjusted to tune the NP synthesis, including temperature, reaction time and the composition of the solution; the latter is expressed in terms of the nature of the precursors, the polyol type, the use of surfactants and additives, and the pH of the medium.

Multistep redox processes occur in the polyol process; for example, in case of ethylene glycol the first step implies that two solvent molecules are dehydrated, to form acetaldehyde. This latter species is then responsible for reduction of the metal precursor, generating Cu NPs and CO_2.

1.3.3.2 Polymer-Based Soft-Template Processes

Several polymers have been proposed as stabilizing agents for the Cu NPs synthesis. Used mixed with water and surfactants, polyethylene glycols (PEGs) have been successfully applied to the preparation of spherical Cu NPs by the group of Zhang [201], while Xie and collaborators obtained junctions of Cu nanorods [202] from a PEG/CTAB soft-template system. Unlike the polyol approach, the polymer species were barely used as modifiers in a soft-template micellar system, whilst the copper reduction was performed by a conventional reagent, such as ascorbic acid [201] or $NaBH_4$ [202].

A similar approach was also used in the case of poly(vinyl alcohol) (PVA). In 1999, Wang *et al.* used a soft-template method based on PVA/isopropanol/water micelles, and operated the $Cu^{(II)}$ reduction by means of borohydride [203]; more recently, Khanna *et al.* obtained Cu NPs in PVA/water emulsions, by employing hydrazine hydrate or sodium formaldehyde sulfoxylate as reducing agents [204].

It should be noted here that the use of polymer/surfactant complex mixtures such as those proposed in Ref. [202] seems particularly promising, due to some additional advantages. Surfactants associated with a polymeric additive may form micelles at concentrations considerably lower than those required by the surfactant alone. Moreover, in the case of polymer/surfactant mixtures, stabilization of the inorganic crystals may benefit from synergetic capping effects that improve both morphological stability and homogeneity [202].

Poly(vinylpyrrolidone) (PVP) is certainly one of the most investigated polymeric additives for the template Cu NP synthesis, having been employed in aqueous [205–208], amide [209], polyol [210–214] and alcohol solvents [215, 216].

In the first of these cases, spherical NPs were easily obtained by conventional reduction of a $Cu^{(II)}$ salt in the presence of alkaline borohydride [205, 207] or ascorbic acid [206] aqueous reducing solutions. Recently, a continuous and steady-flow reactor was proposed, in which a metal displacement reaction occurred. Basically, this involved a spontaneous redox reaction between $Cu^{(II)}$ ions and an oxidizable metal foil, carried out in the presence of PVP and under hydrodynamic and mechanical assistance [208].

Interestingly, processes involving the use of polyol/alcohol solvents appear as a form of modified/improved version of the polyol method, in which the polyol/alcohol solvent is assisted by a specific (and generally stronger) reducing agent, such as hydrazine [215, 216], sodium phosphinate monohydrate [212] or ascorbic acid [210, 211]. The simultaneous presence of PVP and solvents with alcoholic moieties made it possible to obtain monodisperse copper nanocubes [211], nanoparticle arrays and aggregates [216] or nanorods [216], as a function of the experimental conditions.

The good morphological stability and size homogeneity of PVP-capped Cu NPs was exploited in several applications, including reusable catalysts [209] and nanocopper-based conductive ink-jet printing [212]. However, the use of PVP/Cu NPs in catalysis suffers severe limitations in terms of particle activity due to the strongly coordinating capping agent, and this often compromises the NP activity [1].

1.3.3.3 **Encapsulation in Dendrimers**

Dendritic molecules are repeatedly branched species with a symmetric and monodisperse structure and chemical composition [217–219]. Since the late 1990s, they have been shown to be useful template structures for the controlled synthesis of metal NPs [1, 220] and, particularly, of Cu NPs [221–224]. In one of his outstanding papers on this subject, R.M. Crooks defined the approach based on dendrimers as a “ship-in-a-bottle” route to obtain transition-metal NPs [221]. Interestingly, the dendrimer behaves as a monodisperse nanoreactor and allows the preorganization of the metal into its inner part. Basically, the process is based on a strong interaction between $Cu^{(II)}$ ions and the dendrimer core. It has been shown that the number of metal atoms adsorbed into the dendrimer inner part corresponds to the number of tertiary amines present therein [221], although nonspecific surface complexation may occur leading to undesired phenomena such as NP aggregation. Subsequently, the metal ions become entrapped in the template structure, while a conventional chemical reduction of the metal–dendrimer complex (e.g. by means of $NaBH_4$) induces the formation of a nanosized inorganic core inside the dendrimer shell (Figure 1.19).

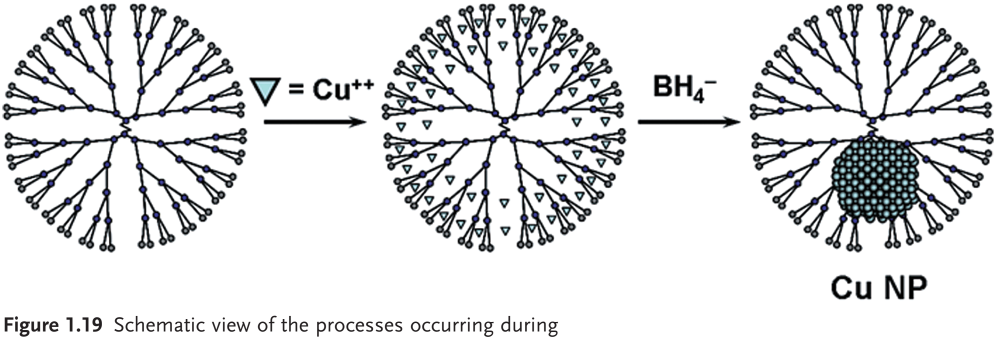

Figure 1.19 Schematic view of the processes occurring during the formation of Cu nanoparticles in a dendritic structure.

The main studies on dendrimer-stabilized Cu NPs relate to capping agents derived from just two structures, namely poly(propylene imine) [221, 222] and poly(amido amine) [223, 224].

1.3.4
Wet-Chemical Routes Based on Biotemplate Systems

Since the late 1990, templates consisting of biomolecules such as DNA have been investigated as a tool to produce elongated metal nanostructures, eventually aiming at the 'bottom-up' assembly of functional nanocircuits [225]. A few years later, in 2003/2004, DNA-templated copper nanowires were obtained by Wooley and colleagues [226, 227], the approach consisting of a time-controlled reduction of aqueous $Cu(NO_3)_2$ by ascorbic acid, in the absence of light, and in the presence of double-stranded DNA. Previously, the latter species had been bound electrostatically to a silicon substrate and mechanically aligned [228], as the authors had envisaged an ultimate application of Cu nanowires as interconnections in nanoscale integrated circuitry [226].

Methods to prepare elongated ensembles of copper NPs that had been generated on the surface of tubular templates were proposed by the groups of Matsui [229] and Wei [230]. Matsui's group, in 2003, studied the growth of Cu nanocrystals on the histidine-rich surface of peptide nanotubes. The Histidine moieties behaved as ligands for $Cu^{(II)}$ entrapment on the nanotube surface, after which a conventional borohydride reduction allowed Cu NPs growth (Figure 1.20). Similarly, in 2005, Wei and colleagues synthesized tubular glycolipid–copper nanotubular complexes which acted as a template for the subsequent thermal preparation of aligned Cu NP arrays (Figure 1.21).

Template methods based on microorganisms (or even plant roots) have also been proposed. In the former case, the 4 nm-wide inner channel of tobacco mosaic

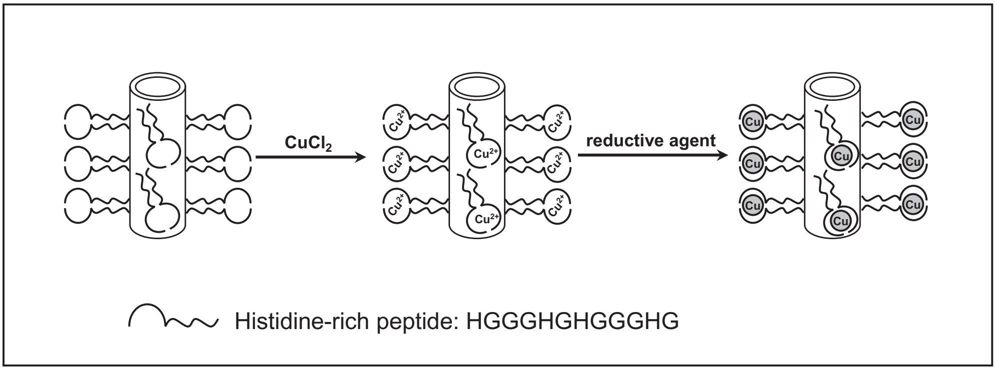

Figure 1.20 Scheme of copper nanotube preparation. From left to right: Cu ion–HG12 peptide complexation on the nanotube surfaces; Cu nanocrystal growth on the nanotubes nucleated at Cu ion-binding sites after reducing trapped Cu ions.

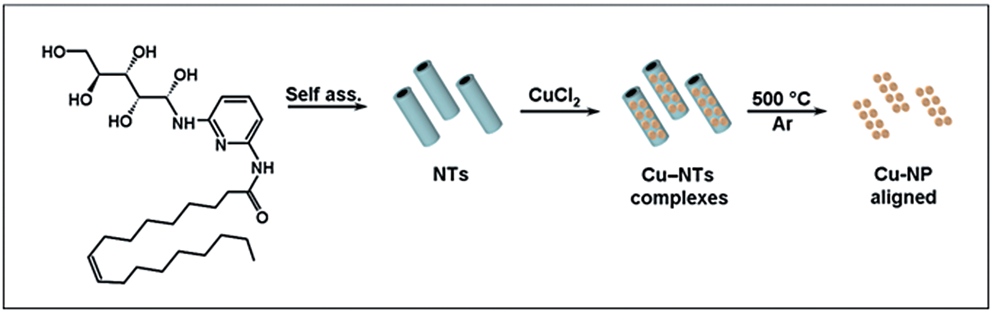

Figure 1.21 Glycolipid-template synthesis of aligned Cu NPs. NTs = nanotubes.

virus (TMV) allowed the preparation of copper nanowires [231]. A similar approach was followed by Demir *et al.* [232] in 2003, who photochemically reduced Cu species on the TMV surface such that ultimately the Cu NPs decorated the outer virus surface. Finally, in a recent study, Manceau *et al.* showed that Cu NPs could be generated at the root–soil interface [233].

1.3.5
Redox Routes in Compressed and Heated Fluids: Hydrothermal, Solvothermal and Supercritical Fluid Methods

The term ‘hydrothermal’, which is of geological origin, was first used by Sir Roderick Murchison during the nineteenth century to describe the action of water at high temperature and pressure, on the Earth’s crust, leading to the formation of rocks and minerals. In a more modern definition, the same term is associated with any heterogeneous reaction occurring in the presence of aqueous solvents or mineralizers under high-pressure and -temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions [234]. The term ‘solvothermal’ indicates an analogous process that is carried out in a generic nonaqueous solvent, including nonconventional media such as supercritical fluids (SCFs). Other, wider, definitions have also been proposed [234].

The various use of these terms is influenced by the customs of different research communities; for example, chemists and material scientists working in the supercritical region prefer explicitly to use the term ‘supercritical fluid’ to characterize their approach. As a consequence, in this section we have maintained a distinction among purely *hydrothermal* (e.g. water-based), *solvothermal* (e.g. based on other solvents) and *SCF* processes, although in some cases this classification might be found controversial, or based on terminological and/or usage rather than substantial differences.

1.3.5.1 Hydrothermal Routes

Because of the highly controlled diffusivity in a strong solvent medium and in a closed system, hydrothermal/solvothermal techniques offer interesting advantages in the processing or preparation of nanomaterials.

Knowledge of the fundamental aspects that drive hydrothermal/solvothermal processes has increased in recent years, and a solid understanding of changes in solvent parameters (e.g. structure at critical, supercritical and subcritical conditions, dielectric constant, pH, viscosity, density, etc.) under hydrothermal conditions, as well as on changing pressure and temperature, is considered a key aspect for programming experimental approaches, as they influence the solubility and transport behavior of the precursors involved in liquid–solid NP synthesis.

Of note, most of the studies which have dealt with the hydrothermal preparation of copper nanostructures have produced elongated or wire-like materials. One of the first applications of this approach was described by Liu *et al.*, who carried out the hydrothermal reduction of a $Cu^{(II)}$–glycerol complex in the presence of phosphite and SDS (used as capping agent). As a result, a wire length of several tens of microns was obtained [235]. A few years later, the group of Zheng [236, 237] used ascorbic acid as reducing agent and PVP as capping agent, for the one-step hydrothermal synthesis of Cu nanorods with rectangular cross-sections (a form of 'French fries' morphology), whereas the groups of Zhang and Huang both showed that ultralong Cu wires could be respectively obtained by using vitamin C [238] or octadecylamine [239]. In both studies, the additive had the dual role of reducing and capping agent. Carbon-coated Cu nanocables were obtained by Deng *et al.* using CTAB and hexamethylenetetramine [240].

Spherical [241] or platelet-shaped [242] Cu NPs could also be prepared. In the former case, glucose was used as reducing agent and CuO particles as precursor, whereas in the latter case hypophosphite and SDS were used to hydrothermally convert $Cu^{(II)}$ ions into elongated nanoplatelets.

1.3.5.2 **Solvothermal Routes**

Several solvents have been tested for the solvothermal preparation of Cu nanostructures. In particular, ethanol was employed as both solvent and reducing agent in the studies of Tang *et al.* [243] and Wei *et al.* [244]. In the former study, which was carried out in the presence of PVP, a shape control over spheres and cubes was possible. However, in both studies the experimental approach proved capable of producing $Cu^{(0)}$ or Cu_2O NPs, as a function of the experimental conditions. Higher temperatures and higher alkali concentrations generally lead to the elemental oxidation state, whereas the opposite conditions lead to cuprous oxides [243]. In a similar study, carried out in ethanol with the additional use of CTAB, Wang *et al.* obtained Cu nanowires [245]. When ethylene glycol [246], polysilane [247] and ethylenediamine [248] solvents were also investigated, the studies led prevalently to micron or submicron particles [246, 248] with crystalline structures.

1.3.5.3 **Routes Based on Supercritical Fluids**

During the late 1980s, Fulton and coworkers studied the generation of AOT reverse micelles in compressible fluids such as compressed propane or SCF propane [249, 250]. The group of C.R. Roberts extended Pileni's synthesis of Cu

NPs in AOT micelles (see Section 1.3.2) to the case of compressed propane and SCF solvents [251, 252]. The compressed solvent systems provide an alternative approach to thermodynamic control over NP synthesis; moreover, one of the main additional advantages over syntheses that employ conventional liquids is the ease of solvent removal, made possible simply by depressurizing the system [253, 254]. The same group proposed a total interaction energy model to predict the ultimate Cu NP size obtained in SCF solvents, and also provided evidence that, even in these media, AOT acts as a stabilizing agent sterically protecting Cu nanocrystals. From the interaction energy plot of Figure 1.22, it is possible to determine the dispersibility of the particles – that is, the separation distance corresponding to a minimum energy value. The effects on particle stability of NP size and SCF media pressure and temperature are shown in Figure 1.23.

Other authors investigated the synthesis of Cu NPs in different SCF media. When, in particular, Ziegler *et al.* employed supercritical water and alkyl thiols [255], the latter species were found to behave both as capping and reducing agent, assisting the conversion of $Cu^{(II)}$ precursor and intermediate species into capped $Cu^{(0)}$ NPs (see Figure 1.24).

Wai and collaborators explored also the potentialities of water-in-supercritical CO_2 microemulsions [256] and used sodium AOT and perfluoropolyetherphosphate as surfactants. More recently, Shervani *et al.* [257] proposed the use of a fluorinated analogue of AOT [sodium bis(1*H*,1*H*,7*H*-dodecafluoroheptyl)-2-sulfosuccinate] to create microemulsions in the same water/supercritical CO_2

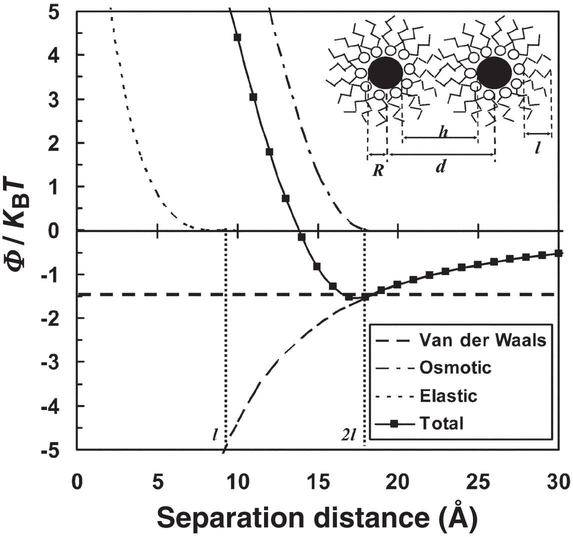

Figure 1.22 Contributions of each force to the total interaction energy model as a function of the separation distance of the particles. Reprinted with permission from *Industrial and Engineering Chemistry Research* **2004**, *43*, 6070–81; © 2004 American Chemical Society.

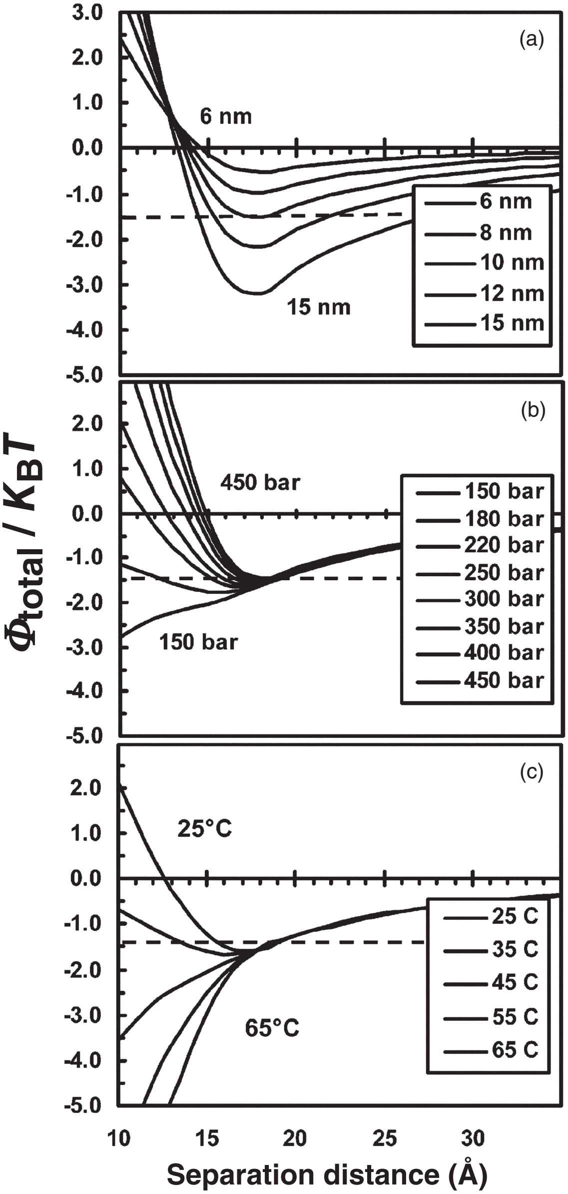

Figure 1.23 Plot of the Φ_{total}/k_BT curves for copper nanoparticles coated with AOT and dispersed in compressed propane. (a) Effect of particle diameter, *f*; (b) Effect of pressure; (c) Effect of temperature. Reprinted with permission from *Industrial and Engineering Chemistry Research* **2004**, *43*, 6070–81; © 2004 American Chemical Society.

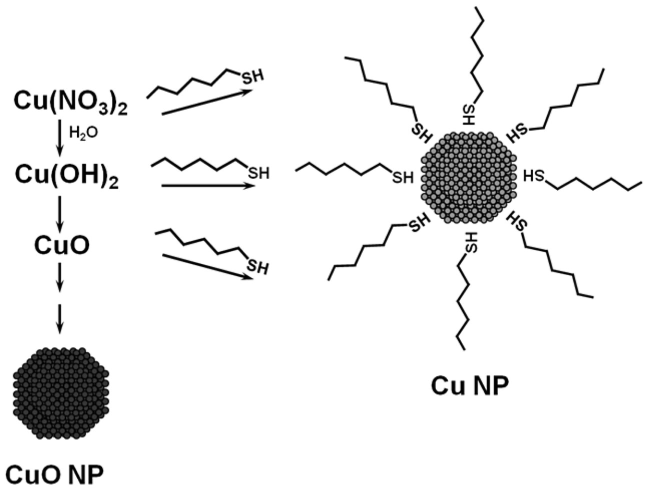

Figure 1.24 Processes occurring during the formation of Cu NPs in supercritical water, in the presence of alkane-thiols.

systems. Both groups used $NaBH_4$ derivatives as reducing agents and were able to obtain spherical Ag and Cu NPs.

Similarly, using alcohol/SCF CO_2/DBS mixed systems, Chen *et al.* converted copper$^{(II)}$ oxalate into Cu nanowires [258]. Cu nanotubes and nanowires were also obtained by Ziegler *et al.* by the SCF decomposition of copper precursors in the presence of mesoporous silica templates [259].

1.3.6
Redox Routes in Ionic Liquids

One valuable approach to NP synthesis and stabilization is via ionic liquids (ILs). Ionic liquids are low-vapor pressure, highly polar and viscous solvents, that have been recently investigated as suspension media for catalytically active nanoclusters [260] (see also Ref. [1] and references therein).The main advantages of synthesizing Cu NPs in ILs resides in the direct possibility of using them as highly recyclable catalysts in several processes, such that there is a low environmental impact (see Ref. [261] and references therein). The so-called 'green' character of such a synthetic approach is that it does not require conventional solvents; rather, separation of the reaction products can be easily achieved by physical treatments, such as distillation inducing solidification of the IL solvent, etc. Furthermore, the IL may itself afford the Cu NP stabilization, thus greatly facilitating catalyst recycling and improving the total turnover (TTO) number. Tetra-alkyl-ammonium halides [261], imidazolium derivatives [262] and other ILs with ammonium moieties [263, 264] have been employed as dispersing media where Cu NPs have been generated and successfully used as catalysts.

In these cases, reduction of the copper precursors was carried out by borohydride [263, 264], by microwave irradiation [262], or even by spontaneous dissolution of macroscopic copper powders (copper bronze) reacting with the counterions of the IL through an oxidation/reduction multistep process that occurs while using NPs in heterogeneous catalysis (as a part of the overall catalytic cycle) [261].

1.3.7
Ultrasonic-Chemical Processes

Ultrasounds often facilitate chemical reactions through an increase of the process kinetics, frequently due to the generation of radicals or other reactive species. Ultrasounds may also provide an unusual reaction medium due to the so-called *acoustic cavitation phenomenon*, which represents the formation, growth and implosive collapse of bubbles in a liquid medium. The discrimination among different effects related to ultrasounds (frequency, intensity and irradiation mode effects) is not easy, and useful insights can be found in a paper by Reisse *et al.* [265]. The first example of Cu nanocrystals synthesis by a sonochemical approach dates back to 1998, when Gedanken *et al.* achieved a sonochemical conversion of copper$^{(II)}$–hydrazine carboxylate into Cu NPs in aqueous medium [266]. Some two years later, the same group proposed a modified method in which the use of a zwitterionic surfactant (cetyltrimethylammonium *p*-toluene sulfonate) made possible the sonochemical preparation of elongated Cu nanostructures stabilized by a surfactant monolayer [267]. More recently, Cu NPs and nanorods were prepared sonochemically by the replacement reaction of copper 2-ethylhexoate with sodium in a paraffin solution [268]. More complex approaches to the sonochemical preparation of Cu NPs have also been proposed, based on a combination of sonochemistry and spray pyrolysis [269], the use of an electric plasma discharge in ultrasonic cavitation field [270], or with the use of sonoelectrochemistry [271].

1.4
Photochemical, Laser Ablation and Radiation- or Electron Beam-Assisted Processes

The wet-chemical synthesis of finely and homogeneously dispersed NPs of electropositive metals shows some challenging aspects. As strong reducing agents must be employed, when the metal precursor undergoes reduction it is possible that such agents are not distributed homogeneously through the solution. This implies local variations in the rates of nucleation and growth, and eventually results in the growth of polydisperse particles [272]. In order to address this problem, several strategies can be employed. Often, strong reducing agents with slow kinetics are used, to enable homogeneous nucleation and growth, but in these processes byproducts generated by the redox reactivity of the reducing agent may contaminate the as-prepared NPs. An alternative approach is based on the photochemical conversion of appropriate copper precursors into Cu NPs, and indeed this may become an important and widespread route as it responds to the need to minimize the amount of byproducts/waste created in the NP synthesis [272]. It should be noted however, that some photochemical approaches are still based on the use of sensitizers, and this makes no substantial difference when compared to the aforementioned open issues related to wet-chemical approaches. In recent years, laser ablation and photofragmentation techniques have attracted great interest and, as they do not necessarily imply the use of additives, they can offer complementary advantages. In this section, the main photochemical routes to Cu NPs will be reviewed, together with other methods involving the use of either an external radiation source (e.g. γ-irradiation) or electron beams. Approaches based on microwave-irradiation are not described specifically at this point, due to the heterogeneity of the experimental conditions (reduction in ILs, polyol approach, etc.). However, a number of interesting reports dealing with this type of irradiation have been reviewed elsewhere in this chapter.

1.4.1
Photochemical Reduction in the Presence of Capping Agents and Sensitizers

In 2002, Kapoor and coworkers reported on the photochemical conversion of $CuSO_4$ into Cu NPs by using UV irradiation (Hg lamp, 254 nm) in the presence of a stabilizing agent such as gelatin [273] or PVP [274]. In both studies, benzophenone was employed as the sensitizer, and its photogenerated ketyl radical was hypothesized as being the species effectively responsible for $Cu^{(II)}$ reduction [274]. In 2002, Murakata *et al.* investigated the preparation of Cu NPs from mixed water/ethanol solutions in the presence of photocatalytically active TiO_2 NPs [275], whilst in 2003 Giuffrida *et al.* used UV irradiation to reduce bis(2,4-pentanedionate)copper$^{(II)}$ ($Cu(acac)_2$) [276, 277]. A spectrophotometric investigation of the process [277] showed that it proceeded through a multistep mechanism. First, it was observed that irradiation induced decomposition of the copper complex, releasing free ligand molecules (H-acac) and generating $Cu^{(I)}$ intermediates. In the overall conversion, H-acac behaved as a sensitizer and promoted the formation of Cu NPs. The NP plasmon resonance absorption was also monitored; some typical spectra are shown in Figure 1.25.

By using the same approach as Giuffrida, Darugar *et al.* prepared Cu NPs from the $Cu(acac)_2$ precursor and studied time-resolved transient absorption phenomena for nanoparticles of 12 and 30 nm. The conduction electron energy relaxation was found to be faster in the smaller particles, whereas fluorescence showed an opposite trend [151].

More recently, Warren *et al.* proposed a different photochemical route, based on the (long-term) ambient light irradiation of $Cu^{(II)}$–thiolate complexes; the result

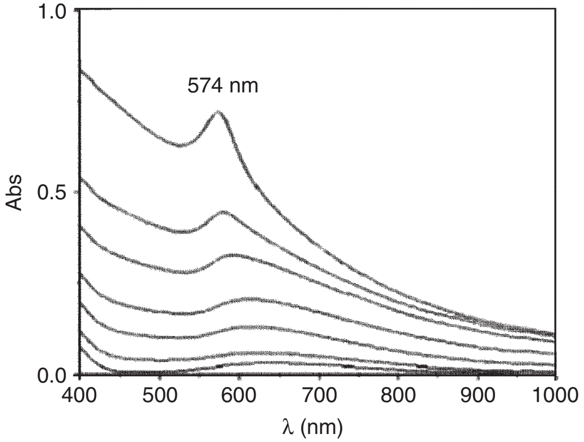

Figure 1.25 Spectral changes recorded upon irradiation of Cu(acac)$_2$ (5×10^{-4} mol l^{-1}) in ethanol solution (at 254 nm) at different times (0–270 min). The light intensity was 5×10^{-6} Einstein min^{-1}. Reproduced with kind permission from © Royal Society of Chemistry; DOI: 10.1039/b308418c.

$$Cu^{2+} + 2\,RSH \longrightarrow Cu(SR)_2 \xrightarrow{h\nu} Cu^0\ \text{NP} + \text{thiol degradation products}$$

Figure 1.26 Sketch of the route proposed by Warren *et al.* (see text for details) for the thiolate-assisted preparation of Cu nanoparticles.

was a complex degradation into metal nanocrystals and disulfide species (Figure 1.26).

1.4.2
Laser Ablation and Photo-Fragmentation Processes

The first examples of the laser ablation (LA) of metal films leading to the corresponding colloid date back to the early 1990s [278, 279]. Unfortunately, in the absence of stabilizers or any other precautions, the as-formed Cu NPs quickly turned into their oxide, leading to the type of olive green-colored solution [280] that those working on Cu$^{(0)}$ NPs (including the present authors!) have experienced disappointedly at least once during their studies.

In the late 1990, research into the LA synthesis of Cu nanostructures followed two roads: (i) depositions in vacuum or under an inert gas; and (ii) LA in the liquid phase.

A brief description of NP formation with LA in an inert gas atmosphere (route# i) is as follows. Initially, interaction between the laser and metal target generates a plume of evaporated atoms that collide with gas molecules at the front of the expanding plume. This causes the plume atoms to thermalize, and a shock wave is initiated that confines the cooling plume; this in turn leads to atom condensation and NP formation. The primarily formed NPs may evolve into larger particles or aggregates, as a function not only of several parameters but also of the metal type [281].

Although, during recent years, several interesting studies on the fundamental aspects have been conducted [282], and papers providing evidence of Cu NPs formation [281, 283] from gas-phase processes have been prepared, during the past few years the technique has mainly evolved towards solution-based strategies.

The first examples of nonoxidized Cu NPs produced by LA in solution were provided by Yeh and collaborators, who converted an isopropanol suspension of CuO powder into Cu NPs by using a Nd:YAG laser [both fundamental (1064 nm) and second harmonic wavelengths were investigated] [284]. A few years later the same authors investigated the effect of thiols on the system [285], while Tsuji *et al.* studied the influence of laser wavelength on the efficiency of ablation of metallic copper targets immersed in an aqueous solution [286].

Subsequently, many studies have been conducted on the Nd:YAG laser ablation of bulk copper [287–289] or $Cu^{(0)}$ powder [290, 291], and on targets in solvents such as water [287, 291], isopropanol [289, 290], acetone [287] and polysiloxane [288]. In Ref. [289], PVP was investigated for the LA preparation of polymer-protected Cu NPs.

Very recently, an excimer laser was used to convert large Cu NPs into finer colloids by a controlled photofragmentation experiment. A TEM evaluation of the Cu NP core-size showed that it was approximately halved upon photofragmentation (10^4 laser pulses) by comparison with the pristine sample [292].

1.4.3
γ-Irradiation

The radiolytic reduction of copper ions in water or alcohols, which has been investigated since the 1970s [293–295], is usually performed by irradiating solutions which contain (besides the copper precursor) a suitable organic compound. The irradiation generates solvated electrons and organic radicals which are then responsible for the reduction of copper compounds to $Cu^{(0)}$ [296]. Several studies have detailed the stabilization of radiolytically prepared Cu clusters by means of polymers such as poly(ethyleneimine) [297], poly(vinyl acetate) [298], PVP [299], or even quaternary microemulsion systems [300]. One example of a mixed radiolytic/hydrothermal approach was proposed in 1994 [301]. Two recent studies have been carried out in the presence of alcohols (but without other stabilizers), and have assessed specific aspects of the synthesis mechanism, including the role of alcohol molecules in the scavenging of radical intermediates [296, 302]. Moreover, Henglein investigated a type of seeded-growth phenomenon in which γ-irradiation-generated Cu NPs were exposed to a fresh precursor solution, after which the mixed liquid was irradiated again, thus inducing an appreciable size increase in the pristine clusters [296].

1.4.4
Electron Beam Irradiation

Similarly to the situation in γ-irradiation, in aqueous solution the use of electron beams generates hydrated electrons and hydrogen atoms, both of which are highly active reducing agents [303–305]. These species have been successfully applied to the preparation of Cu nanocolloids, especially in the presence of stabilizers such as poly(vinyl alcohol) [304] and SDBS [305].

Another (quite exotic) route employing electron beams, which dates back to the 1980s [306, 307], consists of the small-scale preparation of Cu nanostructures by the controlled beam reduction of oxidized copper structures in a TEM instrument. In 2004, Chiu and collaborators used a convergent electron beam to induce the growth of $Cu^{(0)}$ structures from commercial CuCl crystals supported on TEM grids [308]. One year later, Schmittel *et al*. employed $Cu^{(I)}$-bisphenanthroline scaffolds to obtain pure crystalline Cu NPs [309]. Given these evidences, it might be considered straightforward – or even obvious – to turn oxidized copper materials into their elemental oxidation state while exposing them to a TEM electron beam.

In contrast, in 2003 Wang *et al.*, who previously had achieved the structural evolution of $Cu(OH)_2$ nanobelts to Cu nanowires in a TEM instrument, showed that the process was not induced by the electron beam but rather was a multistep process that involved hydroxide thermal dehydration and two subsequent one-electron conversions, in which carbon from the supporting grids acted as the reducing agent [310].

1.5
Electrochemical Approaches

Electrochemical procedures have not been used extensively for the synthesis of metal nanoparticles, despite possessing certain important advantages over other techniques. Yet, electrochemical procedures are of great interest as they not only afford high-purity products but also permit a strict control over the cluster morphology, that can be achieved by varying either the current density or the applied potential.

During the past two decades a variety of different electrochemical methods have been described for the preparation of metal nanostructures of different sizes and shapes. Among these, the most frequently used methods to prepare unsupported $Cu^{(0)}$ nanomaterials have included:

- Sacrificial anode electrolysis in the presence of surfactants
- Electrochemical milling
- Ultrasonic–electrochemical methods
- Electrolysis in ionic liquids
- Template-assisted electrosynthesis of Cu nanorods and nanowires.

Despite electrodeposition techniques, both pulsed and continuous, represent the most widespread and versatile methods for the preparation of nanostructured metals [311–315], they have been intentionally left out of our list. Whilst, on the one hand, these electrochemical procedures enable a tight control on cluster morphology (grain size and shape), on the other hand they usually produce nanostructures that adhere to the electrode surface. Here, only procedures which lead to unsupported nanostructures, or supported nanostructures that are easily removable from the template, have been considered. The above-listed approaches will be reviewed in the following sections, with emphasis placed on the advantages of each method and the properties of the nanostructures.

1.5.1
Sacrificial Anode Electrolysis in the Presence of Surfactants

One valid alternative to the electrolytic deposition of metal clusters is the direct electroreduction of metal ions in the presence of an appropriate stabilizer capable of preventing particle adhesion to the electrode surface. Such stabilizers adsorb onto the growing particles, thus preventing their deposition and producing structures that usually are stable within the reaction environment. These molecules can be chosen from different types of surfactant; a good stabilizing agent should not interfere with the electroreduction of the metal ions, and neither should it passivate the electrode active surface.

This technique is performed using a sacrificial anode experimental set-up, and is referred to as *sacrificial anode electrolysis*. During the process, the stabilizing effect can occur either at the anode or at the cathode. In the former case, the anode is made from the metal to be electrodispersed as nanostructures; when the applied potential is sufficiently high, the anode dissolves into metal ions that subsequently are precipitated due to the presence of hydroxides or other anions [316].

More frequently, sacrificial anode electrolysis is combined with cathodic stabilization; the first report of the electrochemical production of Me-NPs using this technique can be traced back to M.T. Reetz in 1994 [317]. Such studies proved that size-selected nanostructured transition-metal particles could be electrosynthesized using tetra-alkyl-ammonium salts as surfactants, dissolved in organic solvents. This simple electrochemical approach was proposed by the same authors as a general and reliable route to nanosized transition metals, including copper [318, 319]. Following the Reetz studies, the authors of this chapter optimized sacrificial anode electrolysis to prepare copper nanoparticles for several technological applications, including biostatic/biocide nanocoatings [320, 321]. This synthesis was performed by using a three-electrode cell, equipped with an $Ag/AgNO_3$ reference electrode, a copper anode and a platinum cathode. Tetra-*n*-alkyl-ammonium chloride was dissolved ($0.1\,M$) in tetrahydrofuran/acetonitrile mixed solvents; a sketch of the electrochemical cell used in the process is shown in Figure 1.27a.

The correct choice of experimental parameters causes the anode to become electrocorroded during electrolysis, leading to the production of metal ions. The halide–$Cu^{(II)}$ complexes are driven by the electric field to the cathode, where they are electrochemically reduced. The as-formed atoms undergo stages of nucleation and growth, although the presence in the double-layer region of an appropriate

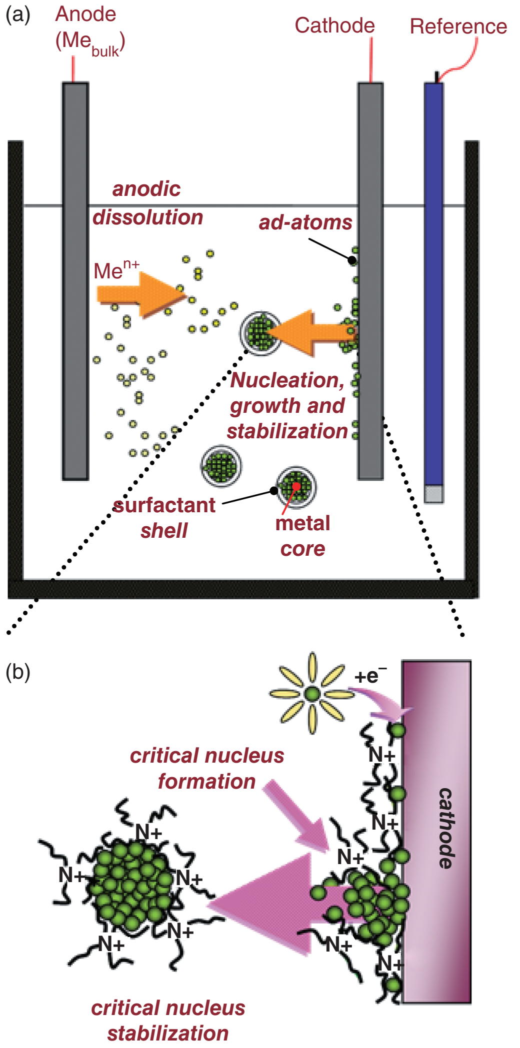

Figure 1.27 (a) Sketch of a sacrificial anode electrolysis; (b) Scheme of processes taking place at the cathode surface.

stabilizer will prevent undesired growth and aggregation. The stabilized core-shell particles are then obtained directly as colloidal NPs in solution (Figure 1.27b).

A variety of different stabilizer chain lengths was explored and potential values applied in order to understand how the experimental conditions can affect NPs size-modulation. The *shell thickness* can easily be tailored by changing the length of the alkyl chains of the surfactant [322], while modulation of the Cu-NPs *core-size* could be achieved only within a very limited size range (diameter <10 nm) by varying the electrochemical parameters. The morphology of the electroproduced nanoparticles was studied using TEM, and their chemical composition determined using X-ray photoelectron spectroscopy (XPS). TEM images of Cu-NPs electrosynthesized at +1.5 and +4.0 V are shown in the insets of Figures 1.28 and 1.29. With NP mean core sizes close to 6 and 3 nm, respectively, these results confirmed the inverse dependence of particle diameter on the applied potential.

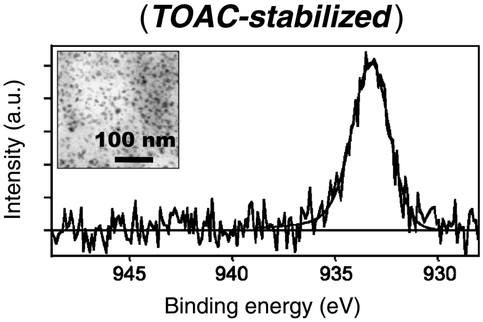

Figure 1.28 TOAC-stabilized Cu NPs electrosynthesized using a working electrode potential of +1.5 V. Main panel: Cu2$p_{3/2}$ XP high-resolution spectrum. Inset: TEM image of Cu-NPs. Reproduced with kind permission from Springer Science + Business Media: *Analytical and Bioanalytical Chemistry*, Synthesis, analytical characterization and bioactivity of Ag and Cu nanoparticles embedded in poly-vinyl-methyl-ketone films. Cioffi, N., Ditaranto, N., Torsi, L., Picca, R.A., De Giglio, E., Sabbatini, L., Novello, L., Tantillo, G., Bleve-Zacheo, T. and Zambonin, P.G., **2005**, *382*, 1912; © 2005 (inset from Figure 1.1; XPS from Figure 1.3).

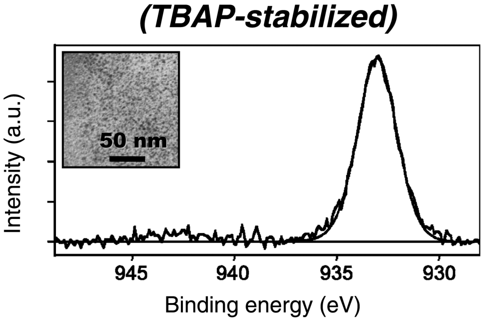

Figure 1.29 TBAP-stabilized Cu NPs electrosynthesized using a working electrode potential of +4.0 V. Main panel: Cu2$p_{3/2}$ XP high-resolution spectrum. Inset: TEM image of Cu-NPs (unpublished results). Reproduced with kind permission from Springer Science + Business Media: *Analytical and Bioanalytical Chemistry*, Synthesis, analytical characterization and bioactivity of Ag and Cu nanoparticles embedded in poly-vinyl-methyl-ketone films. Cioffi, N., Ditaranto, N., Torsi, L., Picca, R.A., De Giglio, E., Sabbatini, L., Novello, L., Tantillo, G., Bleve-Zacheo, T. and Zambonin, P.G., **2005**, *382*, 1912; © 2005 (Figure 1.3).

Typical $Cu2p_{3/2}$ X-ray photoelectron spectra of the same Cu NPs are shown in the main panels of Figures 1.28 and 1.29. It is worth noting that, in the case of the octyl-stabilized clusters (Figure 1.28), the spectrum shows a single peak falling at a binding energy (BE) of 933.1 ± 0.2 eV, this being ascribed to nanodispersed copper at zero oxidation state [323, 324]. In contrast, the signal related to the butyl-stabilized clusters (Figure 1.29) shows the presence of $Cu^{(II)}$ traces, along with nano-$Cu^{(0)}$. In fact, shorter alkyl chains demonstrate a worse ability to protect Cu nanophases against air-induced oxidation, especially upon prolonged exposure to the air [321].

A similar approach was followed by Chen and coworkers in 2003 [325] in the preparation of copper nanorods. These authors used a controlled-current electrochemical method and showed how the shape and yield of the nanorods depended on the current density applied during the electrosynthesis process.

Very recently, sacrificial anode electrolysis was employed by Singh and coworkers to prepare copper nanoparticles in the presence of deoxyribonucleic acid (DNA) as electrolyte [326]. Here, nanoparticles in the range 5–50 nm were synthesized by using a combination of electrolysis and electron-beam irradiation.

1.5.2
Electrochemical Milling

The origin of this approach can be traced back to a surprising byproduct obtained by Tarascon and coworkers [327, 328] during the discharge mechanism of a CuO electrode, when they observed the final product to be nanometer-sized copper grains. This encouraged Chen and coworkers to develop a novel ‘top-down’ method for the synthesis of metal nanoparticles, which became known as the electrochemical milling method (ECM). The process was carried out in an electrochemical cell equipped with a CuO electrode versus a Li counterelectrode; the size and morphology of the nanostructures was tailored by controlling the current density. In this way, copper nanofibers [329], nanospheres and pyramid-like Cu-particles [330] could be obtained (Figures 1.30 and 1.31). The morphology of the particles was shown to depend heavily on the electrode composition and on the number of charge–discharge cycles [330].

1.5.3
Ultrasonic–Electrochemical

Details relating to ultrasound effects were described briefly in Section 1.3.7, with regards to sonochemical approaches. Recently, the potential benefit derived from a combination of sonochemistry and electrochemistry was investigated more fully. Some of the advantages were seen to reside in the acceleration of mass transport and reaction rates, along with increases in the rates of electrode surface cleaning and degassing. Reisse and coworkers [265, 331, 332] have recently prepared copper nanopowders by means of a pulse sonoelectrochemical synthesis, starting from copper$^{(II)}$ sulfate and sulfuric acid. The experiment consisted of two successive

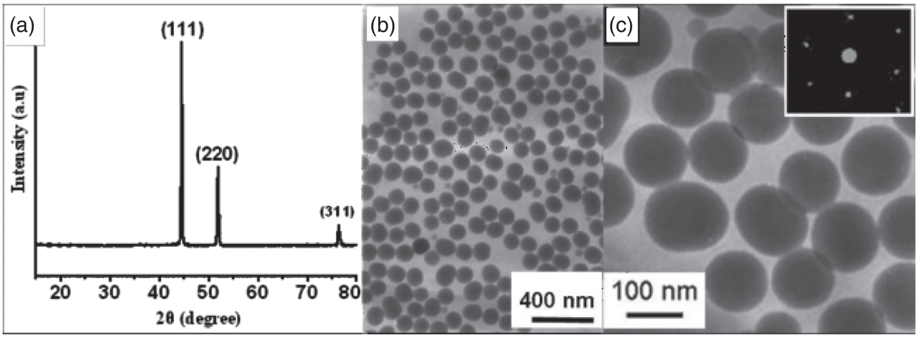

Figure 1.30 (a) XRD pattern; (b) TEM image; (c) High-magnification TEM image of copper nanospheres synthesized after charge–discharge for 50 cycles. The SAED pattern of Cu nanospheres is showed as the inset of panel (c). Reprinted with permission from *Journal of Physical Chemistry C* **2008**, *112*, 4176–9; © 2008 American Chemical Society.

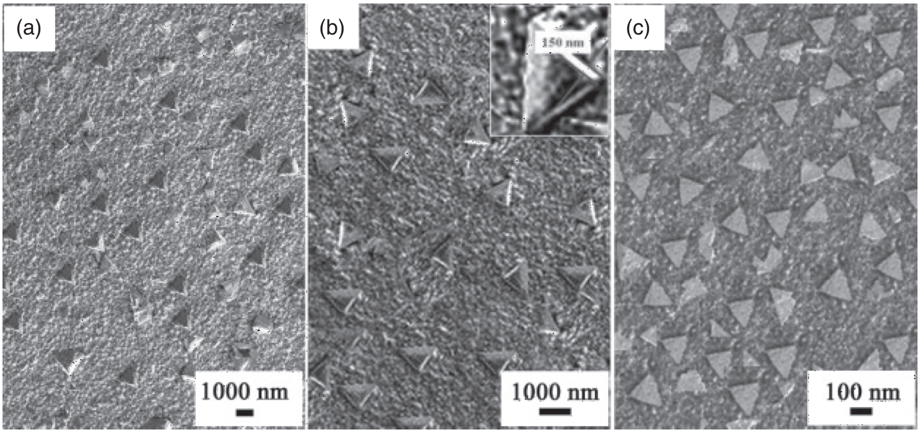

Figure 1.31 Field emission SEM images of the metal copper discharged by Li_2O Cu_2O thin-film electrodes on copper sheet. Panels (a), (b) and (c) refer to particles obtained with different charge–discharge cycles (1, 5 and 50, respectively). A current density of 0.1 mA cm^{-2} was used. The inset in (b) shows a side-view SEM image. Reprinted with permission from *Journal of Physical Chemistry C* **2008**, *112*, 4176–9; © 2008 American Chemical Society.

steps: first, an electric current pulse was applied to the electrode to allow cluster nucleation; second, a burst of ultrasonic energy removed the nanoparticles and micro-metal particles from the sonoelectrode. Later, Gedanken and coworkers developed a modified version of this synthesis by adding a surfactant or a polymer to the sonoelectrochemical cell [271, 333]. CTAB-capped nanosized products resulted in CuBr, while elemental copper nanoparticles were obtained using poly(*N*-vinyl-2-pyrrolidone) and poly(vinyl alcohol) [271].

1.5.4
Electrolysis in Ionic Liquids

This approach basically consists of an electrolytic reduction of copper salts, carried out in a nonconventional IL solvent. The technique exploits electrons as the ‘green’ reductant and the IL as the ‘green’ solvent. In contrast to the relatively narrow potential window of water or other solvents, ILs offer wider electrochemical windows, combined with a stabilizing effect capable of preventing the aggregation of kinetically unstable nanoparticles [334]. Wang and coworkers [335] have recently used this technique for the conversion of CuCl into copper nanoparticles.

1.5.5
Template-Assisted Electrochemical Growth of Cu Nanorods and Nanowires

Metal nanowires and nanorods are considered to be appealing nanomaterials, based on their interesting electronic and optical properties, and their possible application in nanodevices. As a result, the number of papers describing one-dimensional (1-D) metal nanostructures has grown exponentially during the past few years [2]. Today, 1-D nanocopper, in particular, is receiving a great deal of attention due to its high electrical conductance and consequently wide perspective of applications in fields such as microelectronics [336].

A search through *Chemical Abstracts* shows that the most widely used method to prepare metal nanowires and nanorods is based on template-directed electrochemical protocols. The reason for this resides in the advantages deriving from this technique – it is easy to perform, and it affords good control over the crystallinity of nanostructures and their composition. Moreover, key morphological parameters – the nanostructure length and aspect ratio – can be tuned by choosing the correct membrane geometry.

The first study to describe this approach can be traced back to a report by Penner and Martin, who studied the deposition of Pt-nanowires into the pores of alumina [337]. Subsequently, the method was investigated in great depth by several other groups, and recently employed specifically for the preparation of Cu nanorods, nanotubes and nanowires [338–343]. In fact, almost all template electrochemical depositions lead to supported or membrane-embedded nanostructures. As mentioned in Section 1.1, the aim of this chapter is to review only self-standing nanomaterials, and for this reason in the following sections particular attention will be paid to those approaches targeted at the production of unsupported nanomaterials, such as those which include an additional step to dissolve the membrane.

Investigations have been conducted with polycarbonate track-etched templates, aluminum oxide membranes and nonporous mica [344–352], and in all cases the nanomaterial preparation consists primarily of a controlled electrodeposition of copper from a precursor solution (usually $CuSO_4$) inside the nanochannels of the template. In a second step, the template is removed, thus releasing the elongated nanostructures. By following this approach, Gao and coworkers [353] prepared dense and continuous copper nanowires which were 30 μm long and had a uniform diameter of 60 nm. Similar results were obtained by Zheng and coworkers [354], although in this case the nanowires presented a lower aspect ratio. Very recently, Haber and coworkers [343] investigated the effect of deposition parameters on the growth and uniformity of copper nanowires: in particular, they showed that the wave shape and pulse height could not only induce membrane damage but also affect the pore-filling and the resultant uniformity of the nanowires.

The same authors also investigated the possibility of developing voltage-controlled deposition sequences for the set-up of a bench-top electrochemical method capable of producing copper nanowires on the gram scale [355]. In the same report they also showed how the method of wire liberation significantly influenced their diameter and dispersion. Four scanning electron microscopy (SEM) images of Cu nanowires obtained by membrane dissolution under acidic or alkaline conditions are shown in the upper part of Figure 1.32. The simplified scheme shown in the lower part of the figure outlines the differences between the two treatments – that is, when aqueous H_3PO_4 is used the nanowires have a larger diameter and show a greater degree of aggregation.

A further means of gaining control over the diameter and diameter-dependent optical properties of Cu nanowires was proposed by Duan and coworkers [356], who identified a relationship between nanowire diameter and template etching time. By following this approach, they obtained Cu nanowires with a peculiar X-ray diffraction (XRD) pattern, which was suggestive of a preferential growth direction. They also observed a significant red-shift of the surface plasmon resonance peak as the wire diameter was increased.

Nanowires grown by the use of template-directed protocols usually possess a high degree of crystallinity. In particular, Gao and coworkers [353] demonstrated that a suitable choice of potential values during electrochemical deposition allowed the predictable synthesis of either single-crystal or polycrystalline copper nanowires.

1.6
Conclusions

In this chapter we have provided a 'bird's-eye view' of the main approaches for the synthesis of $Cu^{(0)}$ nanosized structures, together with characterization data regarding their morphology, structure and surface chemical composition.

As outlined in the Introduction, academic and industrial interest towards nanocopper is increasing exponentially and a vast number of papers and patents have been published during only the past two years. This represents part of a major trend that is evident in the case of many other transition metals. We believe that, in comparison with other nanosized metals, copper nanostructures may play a crucial role in the development of real-world applications, due to their relatively low cost (as compared to palladium, platinum, gold), and to the widespread use of copper (in other size ranges) in microelectronics and other technological applications. Unfortunately, such potential is counterbalanced by

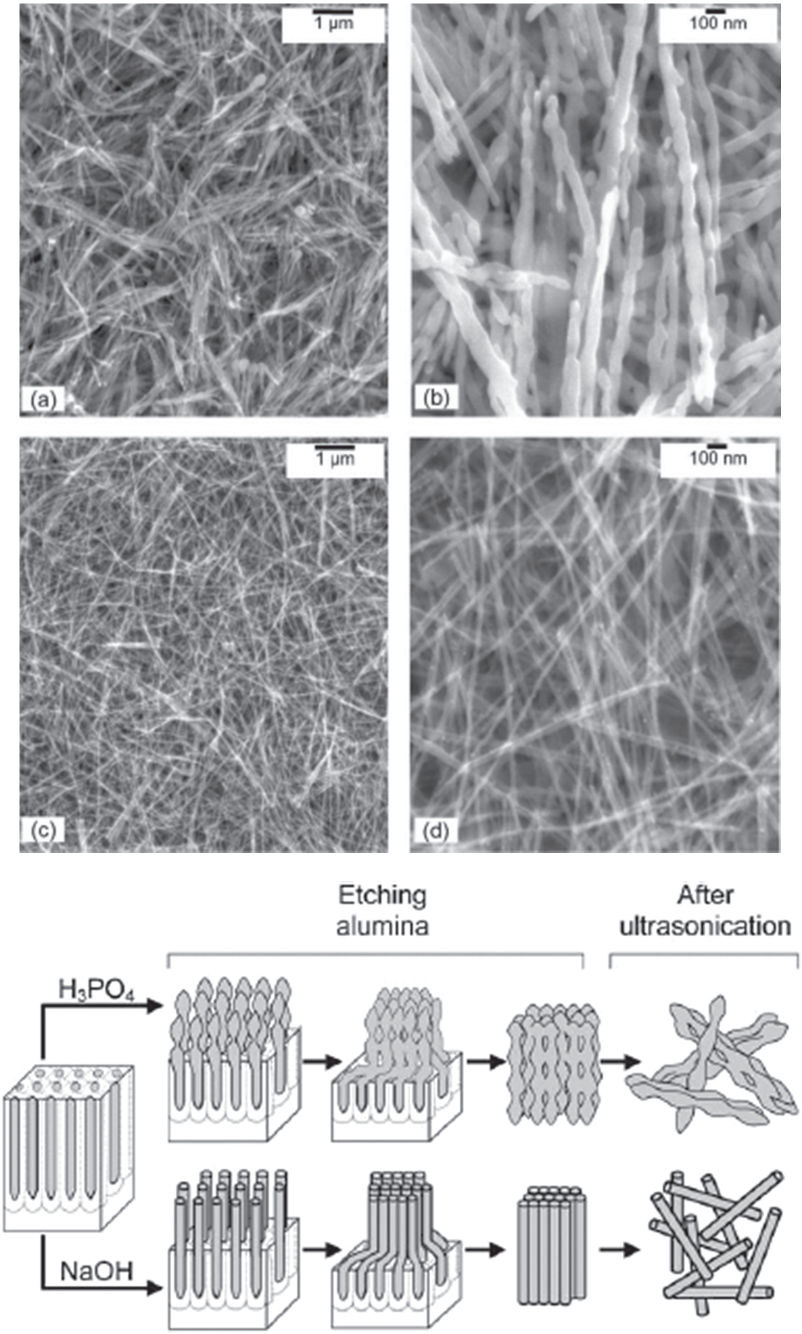

Figure 1.32 SEM images of (a) and (b) acid-liberated copper nanowires and (c) and (d) base-liberated copper nanowires. The lower part of the figure shows a scheme of the liberation process effect on the wire morphology. Reproduced with kind permission from © Royal Society of Chemistry; DOI: 10.1039/b603442j.

the pronounced instability of nanocopper towards degradation processes related to air-exposure.

Many present worldwide efforts in Cu nanomaterials synthesis have been shown to be directed towards the stabilization of nanostructures, aiming at morphologically, structurally and chemically homogeneous nanoparticle populations with an increased preservation of the elemental oxidation state. The interest towards *stability issues* – allowing the correct storage, handling and use of Cu nanomaterials, without having to use excessive precautions – will undoubtedly be intense over the next few years.

As the size of electronic devices continues to shrink with such rapidity, the number of investigations into elongated copper nanostructures such as nanorods (NRs) and nanowires (NWs) will surely increase, especially as both NRs and NWs are expected to play essential roles in future generations of electronic devices [357]. Indeed, NRs and NWs could become the new building blocks for the assembly of nanocircuitry; moreover, in the case of biocompatible or biologically derived capping agents (e.g. amino acids, peptides, DNA strains), aligned and self-assembling copper structures might even be used as a tool for the small-scale biointegration of microelectronic artificial components into living systems.

Today, copper nanoparticles are attracting much interest as low-cost heterogeneous catalysts for several chemical reactions, and have been also shown to provide excellent results when used in green-chemistry applications, such as those involving highly recyclable supported nanoparticles or ionic liquids. It is highly likely that this area of investigation will also undergo major development.

Finally, we would like to describe a potential real-world application of stabilized copper nanomaterials that, at present, we are studying in our laboratory. We have found that Cu NPs capped by quaternary ammonium salts can be used as nanoreservoirs for the controlled release of Cu^{2+} ions, and can be used in this manner as *tunable disinfecting agents*. The tight control of bioactive ion release is essential when maintaining concentrations that will be efficient in terms of antimicrobial activity, yet not show toxicity towards humans [320]. This key property will surely afford interesting applications in areas such as health care, antibacterial textiles, food-packaging, paints and space exploration.

Clearly, the number of methods available to create nanostructures – both at present and in the future – is vast, and will undoubtedly increase even further during years to come. In this respect, we hope that this chapter will serve as a valuable tool in the classification and understanding of these different methods, as well as provide a state-of-the-art review on advanced $Cu^{(0)}$ nanomaterials.

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