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Research Article

Copper Nanoparticles Prepared from Oxalic Precursors

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The synthesis of nanoparticles of copper metal via a soft chemistry route is presented in this paper. The method is based on the thermal decomposition under nitrogen or hydrogen of oxalic precursors with a well-controlled morphology and particle size. The precipitation of the copper oxalates in a water-alcohol medium allows the submicron size of the precursor grains to be controlled and, consequently, the nanometric size of the metallic copper particles to be determined, as required, between 3.5 and 40 nm. The majority of the final particles are made of pure copper metal although some present a superficial layer of cuprous oxide (Cu_2O).

1. Introduction

Nanoparticles are of great interest in the chemical, electronic, and optoelectronic industries because of the novel properties afforded by their small size and high surface-to-volume ratio. Copper metal nanoparticles are mainly attractive due to their catalytic [1–3], optical, and electrical properties [4, 5]. Depending on the size of particle synthesized, surface plasmon resonance phenomena can be revealed, giving a specific colour to the copper metal [6–8]. However, due to the high reactivity of nanoparticles especially concerning oxidation, pure copper metal is not easy to stabilize. Copper oxide forming at the surface of the metal particles changes their structural properties. Thus, a protective coating is applied on the metallic particles to avoid oxidation [9]. Moreover, to stabilize the nanometric size of the particles, they have generally been encapsulated by different organic or inorganic compounds [2, 4, 5, 7, 8, 10–12]. In the literature, pure metal copper nanoparticles about 15 nm in size have been synthesized coupling chemical and physical methods. The process consists in reducing copper sulphate with hydrazine in ethylene glycol under microwave irradiation [13]. Physical methods can also be employed [3, 14]. For example, laser ablation of a sonicated solution of a commercial copper powder dispersed in propanol gives rise to copper nanoparticles of about 5 to 30 nm in size. However, partial oxidation of copper metal into cupric oxide (CuO) has been observed [14]. Preparation of copper nanoparticles of about 8–12 nm in size by an electron-beam reduction method has also been reported.

Chemical methods based on the reduction of a copper salt by $NaBH_4$ [6] or on spray pyrolysis of a copper precursor using ethanol as a reducing agent [15] give rise to the formation of copper particles with a size of about a few tens to a few hundreds nanometers. In this size domain, formation of an oxide layer can be avoided. In contrast, for a particle size lower than 10 nm, metal copper nanoparticles are unstable in air due to oxidation although they can be conserved in an inert medium [6]. Copper nanoparticle synthesis in compressed liquid and supercritical fluid reverse micelle systems has also been mentioned [16].

Using carbon nanotubes as templates [17], copper-chelating glycolipid nanotubes [18], binuclear copper(II) complexes with cyclodextrins [1], lipid-copper hybrid nanofibers [19], or copper(II) complex colloidal assemblies [20] can yield aligned copper nanoparticles or controlled-size copper metal rods. Depending on the template used, the particle size varies from a few nanometers to a few tens of nanometers. However, the presence of CuO can be detected.

In the present study, we used a soft chemistry approach to prepare metal copper nanoparticles stabilized without coating them. We used, for this purpose, transition metal

Table 1: Chemical parameters used for the synthesis of the copper oxalate powders.

Oxalate powder	Copper nitrate solution	Oxalic acid solution	Addition flow ($L\,h^{-1}$)
OP1	$CuNO_3 \cdot 3H_2O$ ethanol, 83% vol. Water, 17% vol. ($3.33\,mol\,L^{-1}$)	$H_2C_2O_4 \cdot 2H_2O$ water, 100% vol. ($0.5\,mol\,L^{-1}$)	0.6
OP2	$CuNO_3 \cdot 3H_2O$ ethanol, 83% vol. Water, 17% vol. ($3.33\,mol\,L^{-1}$)	$H_2C_2O_4 \cdot 2H_2O$ ethanol, 95% vol. Water, 5% vol. ($0.5\,mol\,L^{-1}$)	0.6
OP3	$CuNO_3 \cdot 3H_2O$ ethanol, 83% vol. Water, 17% vol. ($3.33\,mol\,L^{-1}$)	$H_2C_2O_4 \cdot 2H_2O$ butanol, 100% vol. ($0.5\,mol\,L^{-1}$)	1.8

Table 2: Average length (l), width (w), and l/w ratio of the copper oxalate particles synthesized.

Oxalate powder	OP1	OP2	OP3
Measured particles number	25	50	63
L (nm)	65	47	41
d (nm)	18	10	24
L/d	3.6	4.7	1.7

oxalates which are quite simple compounds. Moreover, copper oxalates are easily precipitated in the form of small particles. They are also decomposed at enough low temperature (about 200°C) to prevent dramatic sintering of the metallic particles formed, and their decomposition gives water and carbon compounds, which do not lead to real human health problems.

The synthesis used in this paper is based on the reduction under pure nitrogen or hydrogen of submicronic copper oxalate powders or partially decomposed oxalic precursors. Microstructural observations were made, and the nature of the phases synthesized was determined by scanning electron microscopy and transmission electron microscopy.

2. Experimental

2.1. Chemical Synthesis

2.1.1. Oxalate Powders. Three chemical precipitations (for parameters see Table 1) gave three oxalate powders hereinafter referred to as OP1, OP2, and OP3. In the procedure, a copper nitrate salt was dissolved at 20°C in a water-alcohol medium. The resulting solution was added under stirring to an aqueous or alcohol solution of oxalic acid kept at 20°C. The precipitated oxalate was separated from the liquid waste by centrifugation at 3.000 rpm for 30 min. The precipitate was washed under stirring in deionised water. After the second washing-centrifugation cycle, the particles, whether OP1, OP2, or OP3, did not sediment and remained suspended in the water. This could be due to the very small size of the grains which would have required faster centrifugation to enable their sedimentation. To disperse the oxalate particles and conserve grain dispersion during the decomposition and reduction steps, one drop of each suspension was deposited on a glass slide and spread with another glass slide to give a very thin layer of liquid that was quickly dried to avoid any agglomeration of the oxalate particles.

Some oxalate powders dispersed on the glass slide were partially decomposed under air at 220°C for two hours.

2.1.2. Copper Powders. The oxalate powders dispersed on the glass slide were reduced under pure nitrogen (99.995%) from 200°C to 300°C for 1 hour.

The oxalates that had been partially decomposed under air at 220°C during 2 hours were further reduced under pure hydrogen (99.995%) at 200°C for 5 hours or at 180°C for 15 hours.

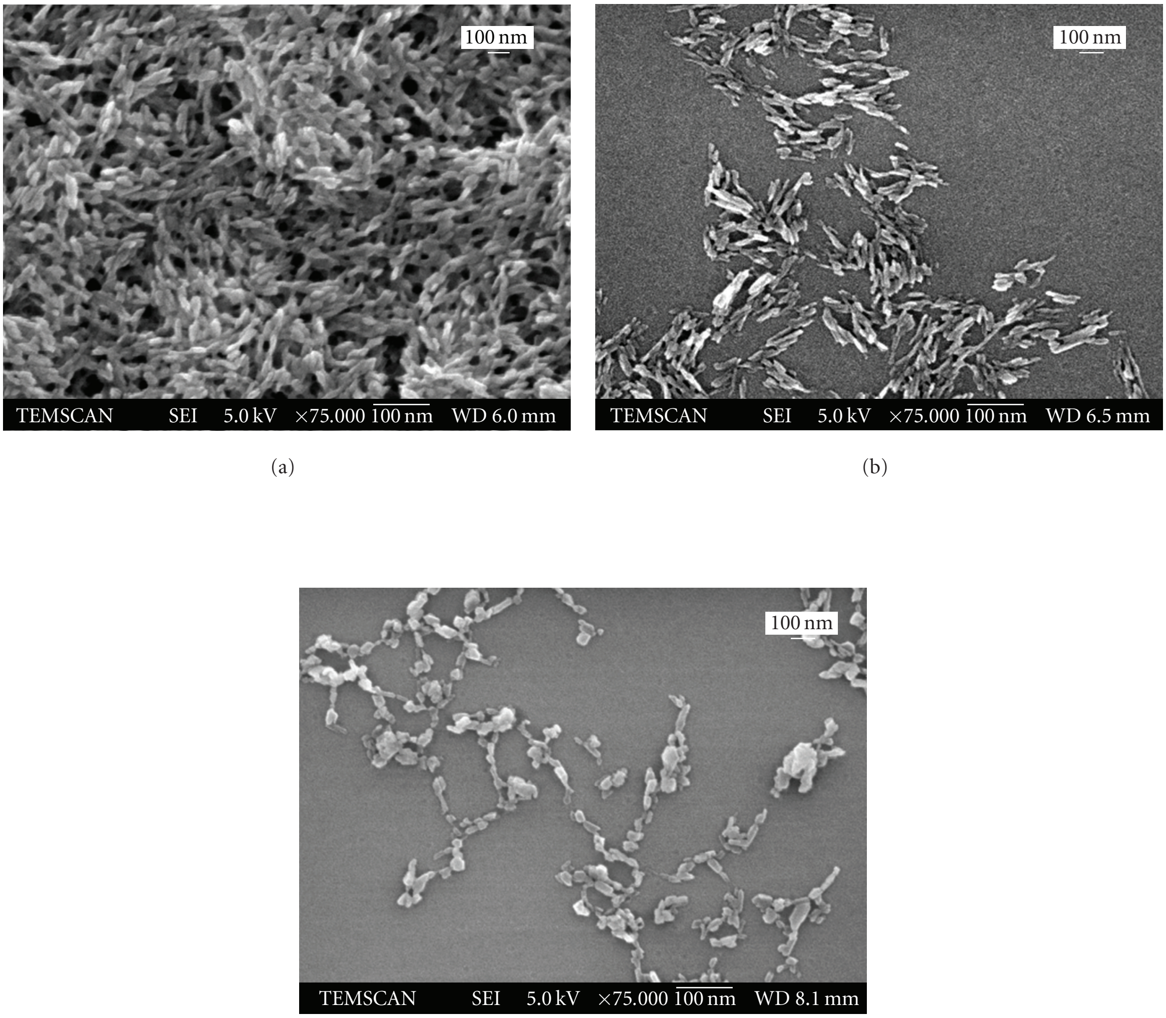
2.2. Characterization. Phase detection was carried out by X-ray diffraction (XRD) pattern analysis ($\lambda_{CuK\alpha} = 0.15418\,nm$). The oxalate powders, partially decomposed oxalates, and metal powders were observed by field emission gun (FEG) scanning electron microscopy (SEM) using a JEOL 6700 F apparatus and by transmission electron microscopy (TEM) using a Jeol JEM 2010 or an FEG 2100 F devices. Phase determination was performed by electron diffraction analysis using a TEM FEG 2100 F apparatus.

3. Results and Discussion

Analysis of the XRD patterns of the three oxalic precursors revealed diffraction peaks of both the anhydrous and the monohydrated copper oxalates: CuC_2O_4 and $CuC_2O_4 \cdot H_2O$.

FEG SEM observations of the oxalate powders showed small elongated particles with a rice-grain shape (Figures 1(a)–1(c)). The length (l), width (w), and l/w ratio of the oxalate particles are reported in Table 2.

The OP3 particles were less elongated in shape than those of the two other oxalates, and, overall, the particle size distribution was larger (Table 2, Figure 1(c)).



(a) (b) (c)

Figure 1: FEG SEM micrographs of the three copper oxalates (a) OP1, (b), OP2, and (c) OP3.

Table 3: Phases from the reduction of the oxalate powders under N_2 atmosphere.

Reduction temperature (°C)	OP1	OP2	OP3
200	$CuC_2O_4 + CuC_2O_4 \cdot H_2O + Cu_2O$		—
250	Cu + traces of Cu_2O	Cu + traces of Cu_2O	Cu + traces of Cu_2O
280	Cu + traces of Cu_2O		
300	Cu + traces of Cu_2O		

Then, OP1, OP2, and OP3 have the same chemical composition, structure, and reactivity, but they display different sizes and shapes.

Heat treatment from 200 to 300°C, under nitrogen atmosphere, was only carried out on the OP1 powder. The results presented in Table 3 show that a temperature of 200°C is insufficient to reduce the oxalate to pure copper metal. The occurrence of Cu_2O, which is an intermediate compound produced during the decomposition of CuC_2O_4 into copper metal, was observed.

Whatever the sample studied, a minimal temperature of 250°C is necessary to reduce the oxalate powder into metallic copper. However, residual cuprite (Cu_2O) was observed whatever the reduction temperature studied (from 250°C to 300°C). This oxide is probably formed on removing the metal powder from the furnace, the contact with air

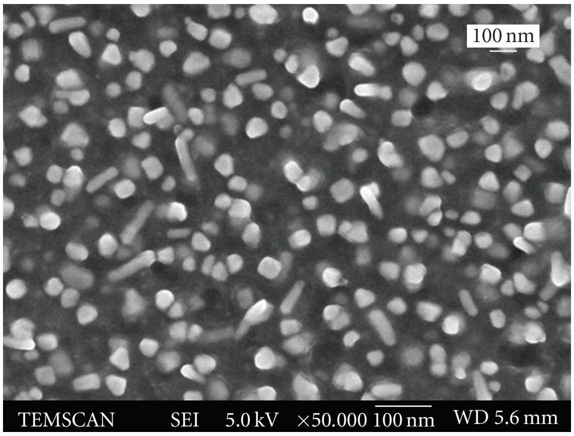


Figure 2: FEG SEM micrograph of the copper particles produced by heat treatment of the OP1 oxalate under N_2 at 280°C.

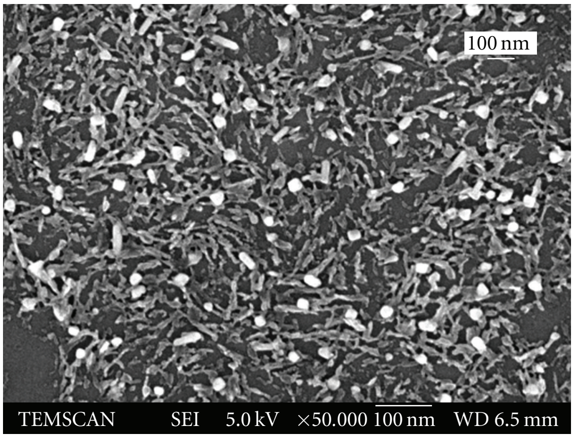


Figure 3: FEG SEM micrograph of the partially decomposed OP2 oxalate reduced under hydrogen at 200°C for 5 hours.

Table 4: Indexation of the electronic diffraction rings of the pattern presented in Figure 8(b).

D (mm)	d (nm)	(hkl) plane
16.25	0.2471	(111) Cu_2O
19.25	0.2086	(111) Cu
22.25	0.1805	(200) Cu
26.25	0.1530	(220) Cu_2O
31.25	0.1285	(311) Cu_2O and (220) Cu
36.75	0.1093	(311) Cu

giving rise to the spontaneous oxidation of the particles' surface.

Copper particles obtained following heat treatment of oxalate OP1 at 280°C under N_2 seem to reveal, in the micrograph in Figure 2, the presence of two populations. The first one could be composed of spherical copper particles between 40 and 100 nm in size while the second could be made up of rods up to 200 nm long. A possibility could exist that the particles are all rodlike, but apparently different morphologies are observed due to projection.

It can be seen that the metal particles are embedded in a carbon gangue (about 0.1–0.3 wt. % C). Carbon is the residue from the decomposition of the oxalate group ($C_2O_4^{2-}$) in the nitrogen atmosphere.

In order to avoid gangue formation, the oxalate powders were decomposed in two steps. First, the oxalic precursors being a mixture of CuC_2O_4 and $CuC_2O_4 \cdot H_2O$ were partially decomposed under air at 220°C for 2 hours to remove most of the carbon and all of water which delays the formation of metallic copper. XRD pattern analysis of the copper oxalates treated in air at 220°C for 2 hours reveals the presence of CuC_2O_4 and CuO.

Total decomposition of the CuC_2O_4 and CuO mixture into copper metal was further performed under hydrogen atmosphere. Hydrogen should react with the remaining carbon to form gaseous products such as CH_4 [21] removed from the furnace by the continuous H_2 flow. Moreover, hydrogen being highly reducing, it became possible to perform the heat treatment below 250°C.

Decomposition of the partially decomposed OP2 oxalate under H_2 at 200°C for 5 hours did not reduce all the CuC_2O_4 and CuO into copper metal. Indeed, the corresponding FEG SEM micrograph (Figure 3) shows the presence of both elongated particles, characteristic of CuC_2O_4 (already presented in Figure 1(b)) and CuO, and spherical particles associated with metallic copper.

In contrast, the XRD pattern of the partially decomposed OP3 oxalate reduced under hydrogen at 180°C for 15 hours indicated the presence of the diffraction peaks of copper metal (Figure 4(a)) and very small amounts of Cu_2O (Figure 4(b)), probably present at the particles' surface.

The dispersed spherical particles were 6 to 23 nm in diameter (Figure 5). Residual carbon was not detected in this sample accounting for the absence of carbon gangue in Figure 5.

The partially decomposed OP3 oxalate reduced under hydrogen at 180°C for 15 hours was noted OP3R. TEM observations were performed on the OP3R particles deposited on 100 mesh carbon-coated Cu grids. The analysis with 0 degree tilt has been performed in the centre of the mesh to avoid the grid contamination. EDX microanalyses (Figure 6(b)) performed on the particles presented in Figure 6(a) reveal the presence of the majority of peaks characteristic of copper. Comparison of copper and oxygen peaks intensities confirms the XRD findings that these particles are mainly composed of copper metal. The presence of oxygen is attributed to Cu_2O probably located at the particles' surface. The peak characteristic of carbon is characteristic of that produced by the grid coating.

The metal particles observed in Figure 6(a) were sized from 6 to 40 nm. The latter value is higher than that measured on the SEM micrographs (about 23 nm). Indeed, in contrast to the SEM observations, both dispersed and agglomerated particles were measured on the TEM micrographs.

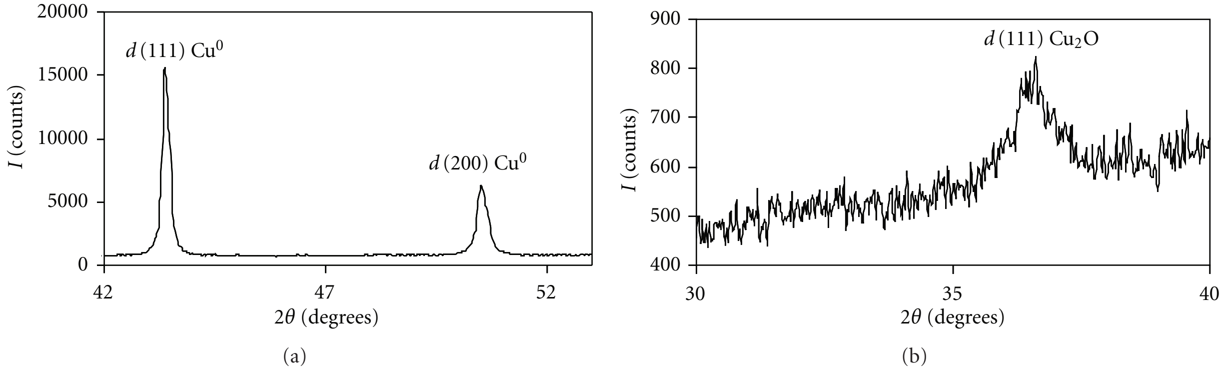


Figure 4: XRD pattern of the partially decomposed OP3 oxalate reduced under hydrogen at 180°C for 15 hours: (a) peaks attributed to copper metal; (b) peaks attributed to Cu_2O oxide (zone enlargement).

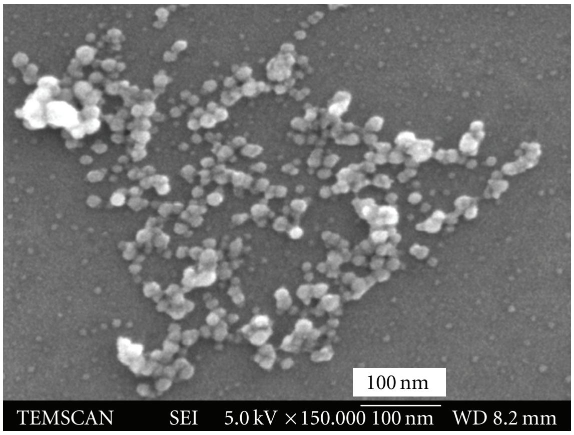


Figure 5: FEG SEM micrograph of the partially decomposed OP3 oxalate reduced under hydrogen at 180°C for 15 hours.

FEG TEM performed on the OP3R sample revealed the presence of very small particles of about 3.5 to 10 nm in size (Figures 7(a)–7(b)). The interplanes distance measured in Figure 7(b) was about 0.210 nm. This distance, near 0.209 nm, is attributed to the (111) plane of copper.

Some particles in Figure 8(a) show a surface layer of thickness that varies for each grain. Electronic diffraction (Figure 8(b)) performed on different areas presenting these coated particles (core-shell particles) always revealed rings attributed to copper metal and Cu_2O (Table 4).

Figure 9 shows one core-shell particle for which the interplanes distance measured in the shell is about 0.250 nm. This value is attributed to the (111) plane of Cu_2O. The interplanes distance measured in the particle core is about 0.210 nm and is related to the (111) plane of metallic copper. These distances, also obtained for other isolated particles, confirm that, when observed, Cu_2O is located at the surface of the copper particles.

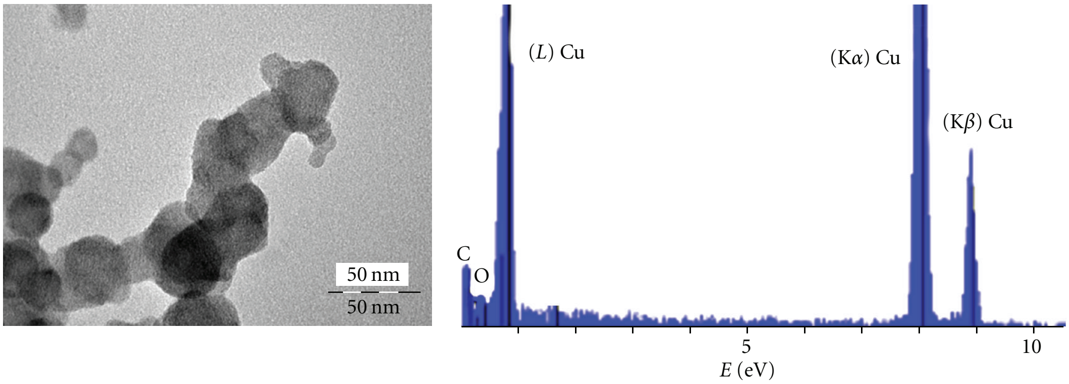
To summarize, our laboratory has developed a facile approach for the chemical synthesis of dispersed copper metal nanoparticles. The process was based on the reduction under H_2 at 180°C for 15 hours of partially decomposed oxalate powders obtained by chemical precipitation. Unlike various other authors [2, 4, 5, 7–12], we did not use coating agents. One population of the particles synthesized is composed of pure copper metal. The other population is characterized by a core-shell microstructure with a shell of Cu_2O oxide at the surface of a copper metal core.

4. Conclusions

Copper nanoparticles were synthesized by thermal decomposition of precipitated oxalic precursors under nitrogen or hydrogen. By acting on the precipitation parameters, anisotropically shaped submicronic oxalate particles were prepared. A precipitation medium composed of water and butyl alcohol gave rise to the smallest particles length (about 41 nm) and l/w ratio (about 1.7). In order to disperse the oxalate particles and to conserve their dispersion during the thermal decomposition steps, the oxalate powders suspended in water were deposited on a glass slide, as a very thin layer, and quickly dried to avoid a particle agglomeration.

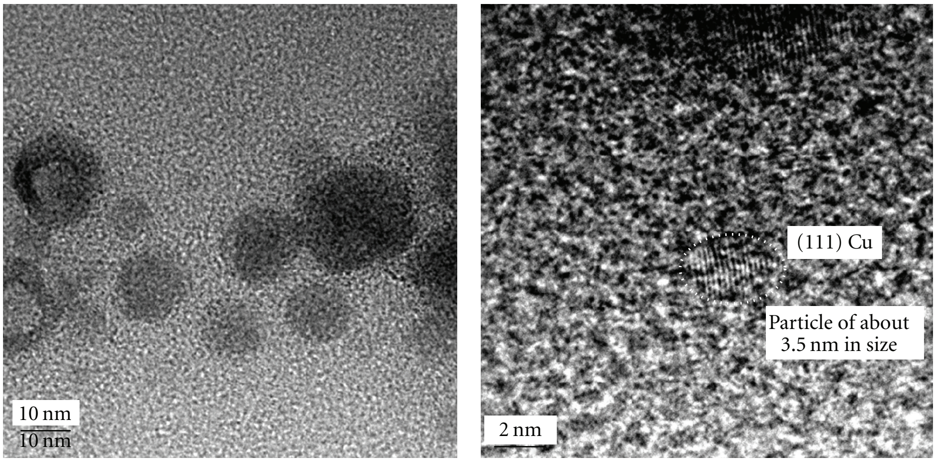
Thermal decomposition under a nitrogen atmosphere revealed that a minimal temperature of 250°C is necessary to reduce the oxalate powder entirely to copper metal. The contact of the metal particles with air gave rise to the formation of Cu_2O at their surface. In addition, the metal particles were encapsulated in a carbon gangue.

In order to avoid gangue formation, the oxalic precursors were decomposed in a two-step process. Heat treatment under air at 220°C for 2 hours was first performed to remove most of the carbon from the oxalate particles and all the water, able to delay the formation of copper metal. A further reduction under H_2 at 180°C for 15 hours yielded copper powder. EDX microanalyses confirmed the presence of both elemental copper and traces of oxygen attributed to a low Cu_2O content. TEM observations revealed the presence of metal particles of about 3.5 to 40 nm in size. Some present a surface layer of varying thickness. Indexation of the electronic diffraction patterns performed on different areas including these core-shell particles revealed the presence of rings attributed to copper metal and/or Cu_2O. The



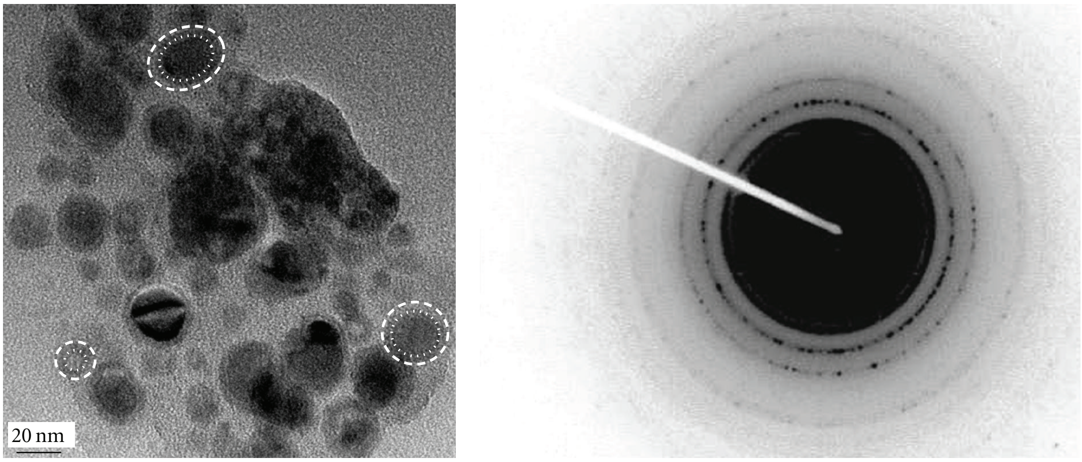
(a) (b)

Figure 6: (a) TEM micrograph of the particles produced by reduction under H_2 at 180°C for 15 hours of the partially decomposed OP3 oxalate (b) corresponding EDX microanalyses.



(a) (b)

Figure 7: FEG TEM micrographs of the particles from the reduction of the partially decomposed OP3 oxalate under H_2 at 180°C for 15 hours: (a) copper nanoparticles; (b) interplanes distance characteristic of the (111) plane of copper metal.



(a) (b)

Figure 8: (a) TEM micrograph of core-shell particles; (b) corresponding electronic diffraction pattern.

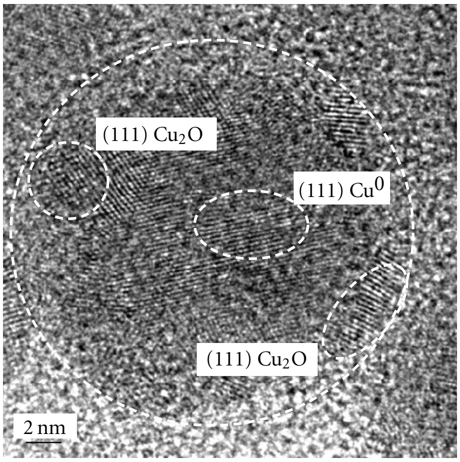


Figure 9: FEG TEM micrograph of a copper metal particle covered with a Cu_2O oxide layer (core-shell particle).

determination of the interplanes distances on some isolated core-shell particles confirmed that Cu_2O was located at the surface of the copper particles.

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