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Copper(I) oxide and metallic copper particles formed in 1,2-propane diol

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Abstract

Chemical composition, particle size, and structure formation of colloidal Cu_2O and metallic Cu synthesized from Cu(II) acetate in an environmentally friendly 1,2-propane diol were studied dependent on the temperature and concentration of the precursor. Cu_2O as a reaction intermediate is formed between 150 and 170 °C, while its reduction to metallic Cu occurs between 170 and 180 °C. Average particle sizes of non-agglomerated Cu powders varied from 100 nm to 1 μm.

Keywords: Powders-chemical preparation; Spectroscopy; Electron microscopy; X-ray methods; Copper

1. Introduction

The synthesis and structure of colloidal metallic copper and its oxide Cu_2O are being studied due to their strong potential for application in catalysis,[1] solar cells[2,3] and the electronics industry.[4,5] Metallic copper is a low cost material with high electrical conductivity which makes it interesting for conductive paths and layers in electronic devices, while Cu_2O is a p-type semiconductor with a strong potential for application in solar cells and batteries. Both metallic copper and Cu(I) oxide also possess substantial catalytic activity. There are several synthetic routes used for their preparation. Among others, they can be prepared by the reduction of precursors in liquid polyols that act simultaneously as a solvent, reducing agent, and medium for preventing particle agglomeration.[6] This synthetic method is known in the literature as a polyol process.[7–9] In the present work we focus on the preparation of Cu(I) oxide and metallic copper particles from nanometer to micrometer size from a Cu(II) acetate ($Cu(Ac)_2$) precursor in 1,2-propane diol. The influence of temperature and concentration of the precursor on particle formation and growth was studied by scanning electron microscopy—SEM, Infrared spectroscopy—IR, and X-ray diffraction—XRD analysis.

2. Experimental

2.1. Materials

Cu(II) acetate, $Cu(CH_3COO)_2{\cdot}H_2O$—$Cu(Ac)_2$ (Merck), 1,2-propane diol, $CH_3CH(OH)CH_2OH$—PD (Merck), ethanol, CH_3CH_2OH—ET (Merck).

2.2. Synthesis procedure

The starting compound, $Cu(Ac)_2$, was dissolved in PD. The solution was placed in a 250 ml reactor equipped with a mixer and reflux condenser, heated at a rate of 7–8 °C/min up to selected temperature, and kept under these conditions until the appearance of a brown red color. The reaction mixture was then cooled and left overnight to settle. The resulting powders were washed twice with ET. After the final washing, the powder was dried in an oven at 70 °C for 2 h. Three series of experiments were performed: in the first one, the precursor concentration was varied while keeping the reaction temperature constant (186 °C). The second and third series were performed at about 175 °C with precursor concentrations of 0.01 and 1.0 mol/l, respectively, in order to follow the reduction of $Cu(Ac)_2$ as a function of time. The designations and important data from the synthesis experiments are summarized in Table 1.

The resulting solids were characterized by three methods. *FTIR spectra* of samples, prepared as KBr pellets, were recorded in transmittance mode on a Perkin-Elmer 1725X spectrometer, in the range from 4000–400 cm^{-1} and at a resolution of 4 cm^{-1}. *SEM micrographs* were obtained on a Zeiss Supra 35VP

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Table 1
Experimental parameters for the reduction of Cu(II) acetate in 1,2-propane diol

Sample designation	C(Cu(Ac)$_2$) (mol/l)	Time (min)	Temperature (°C)	Color of suspension	Crystal size (nm)
Exp 1A	0.004	60	187	Red/brown	–
Exp 1B	0.008	55	187	Red/brown	–
Exp 1C	0.01	65	187	Red/brown	2.95
Exp 1D	0.04	60	186	Red/brown	2.41
Exp 2A	1.0	10	60	Green/blue	–
Exp 2C	1.0	85	178	Green/brown	–
Exp 2D	1.0	120	178	Brown	–
Exp 2E	1.0	200	176	Brown	–
Exp 2I	1.0	360	180	Red/brown	5.58
Exp 3C	0.01	25	175	Green	–
Exp 3D	0.01	30	172	Green/brown	–
Exp 3F	0.01	145	174	Red/brown	6.87

microscope (acceleration voltage 3.37 or 5.0 kV, detectors—in lens/secondary electrons = 0.75/0.25, working distance 3–5 mm, sample preparation—gold sputtering). *X-ray diffraction* analysis was carried out on a Siemens D-5000 diffractometer (source Cu anode, 2Θ range from 2° to 90°, step 0.04°, step time 1 s.), crystallite sizes were calculated by line broadening of (1 1 1) peak of XRD pattern using Scherrer's formula.[7]

3. Results and discussion

Many diols (polyols) are known to reduce various inorganic and organometallic compounds to oxides or even to the metallic state. The most commonly employed diol for this purpose, as reported in literature, is ethylene glycol[8] but others such as glycerol[7] or tetra ethylene glycol[9] have also been used. In this work we show that 1,2-propane diol (PD) also successfully reduces Cu(II) acetate to metallic copper. PD is interesting from a green chemistry viewpoint as it is the most environmentally friendly of the diols and is widely used as a cooling liquid in engines and other devices, as well as in pharmaceutical compositions for oral application as a solvent.[10,11]

The reduction reaction was performed by dissolving the Cu(II) acetate in PD medium by mixing and sonication, and by the subsequent heating and mixing at chosen temperature until the red–brown color of metallic Cu emerged. At a concentration of 0.01 mol/l Cu(Ac)$_2$ was completely dissolved, while at the concentration of 1 mol/l it formed a turbid suspension. The color of the suspension changed during the synthesis from its initial green into green brown and then into brown, resulting finally in the brown red color of the metallic Cu suspension. Samples of the final Cu powders and samples of the reaction intermediates, taken from the reaction mixture, were analyzed by IR, XRD, and SEM.

The morphology, size and degree of sintering of copper particles are mainly dependent on such morphological characteristics of the copper acetate precursor and reaction intermediates as crystallinity, porosity, and degree of aggregation. The influence of Cu(Ac)$_2$ concentration (0.004–0.04 mol/l, Exp 1A–D, Table 1) on the particle structure and average size was determined by SEM microscopy. The average particle size remains practically unchanged at Cu(Ac)$_2$ concentrations from 0.004 to 0.01 mol/l (100–300 nm, Fig. 1(a)), whereas the particle size increases to 0.5–1 μm at 0.04 mol/l. Irrespective of their sizes, the particles are composed of smaller units ranging between 20 and 50 nm (Fig. 1(b)).

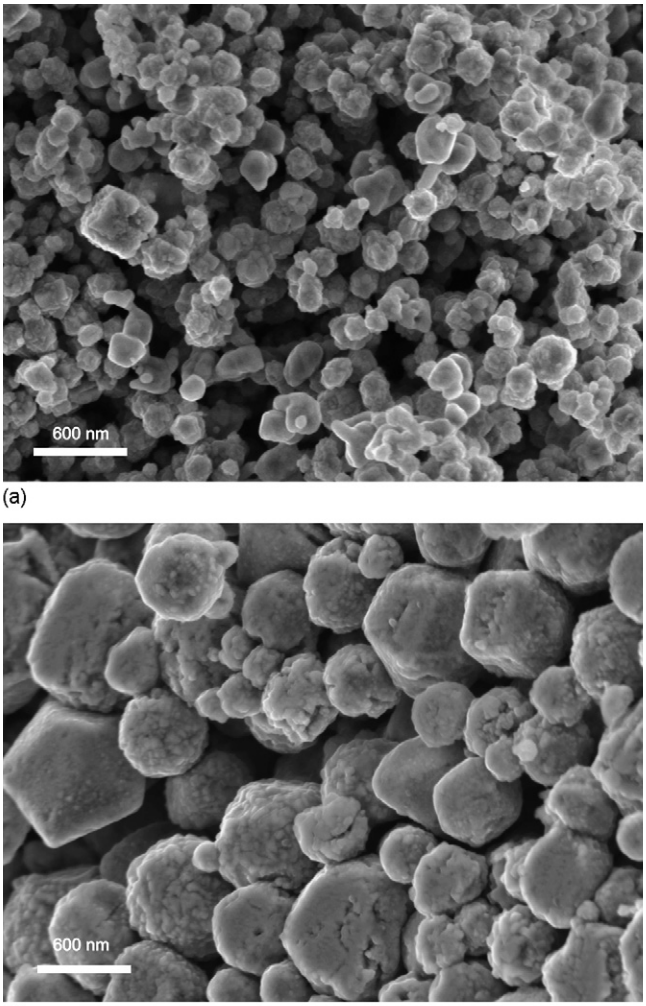

Fig. 1. SEM micrographs of metal Cu particles prepared from different starting concentrations of Cu(II) acetate in PD at 186 °C: (a) concentration = 0.01 mol/l, magnification = 85,000×; (b) concentration = 0.04 mol/l, magnification = 85,000×.

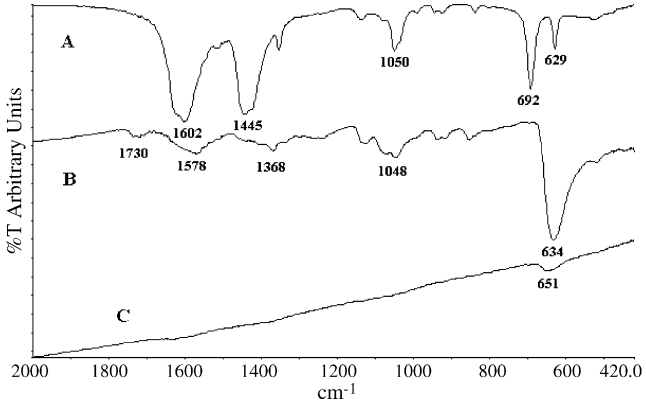

Fig. 2. FTIR spectra of samples taken during Cu(II) acetate reduction in PD: (A) Exp 2A; (B) Exp 2D; (C) Exp 2I (explanation in the text, Table 1).

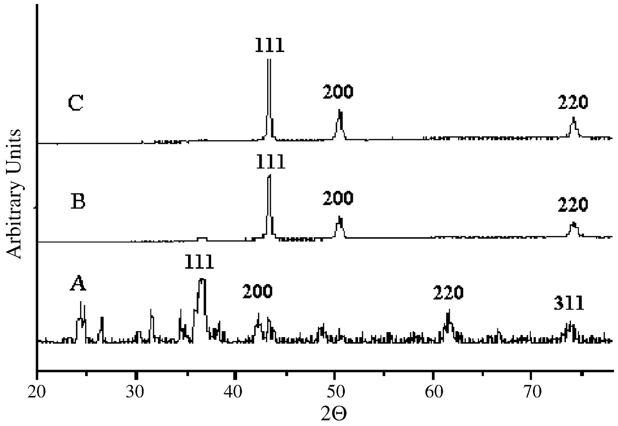

Fig. 3. XRD spectra of samples taken during Cu(II) acetate reduction in PD: (A) Exp 2C; (B) Exp 2D; (C) Exp 2I (explanation in the text, Table 1).

The IR spectra presented in Fig. 2(A) show bands ν_{as} and ν_s of C=O of the acetate group that are in the range from 1680–1530 cm^{-1} to 1490–1360 cm^{-1}, respectively. This means that at temperatures up to 75 °C $Cu(Ac)_2$ is stable. After 120 min the reduction of $Cu(Ac)_2$ is accompanied by the appearance of a new carbonyl stretching band between 1690 and 1760 cm^{-1}, which is characteristic of aldehydes and ketones, and by the appearance of the characteristic absorption band of

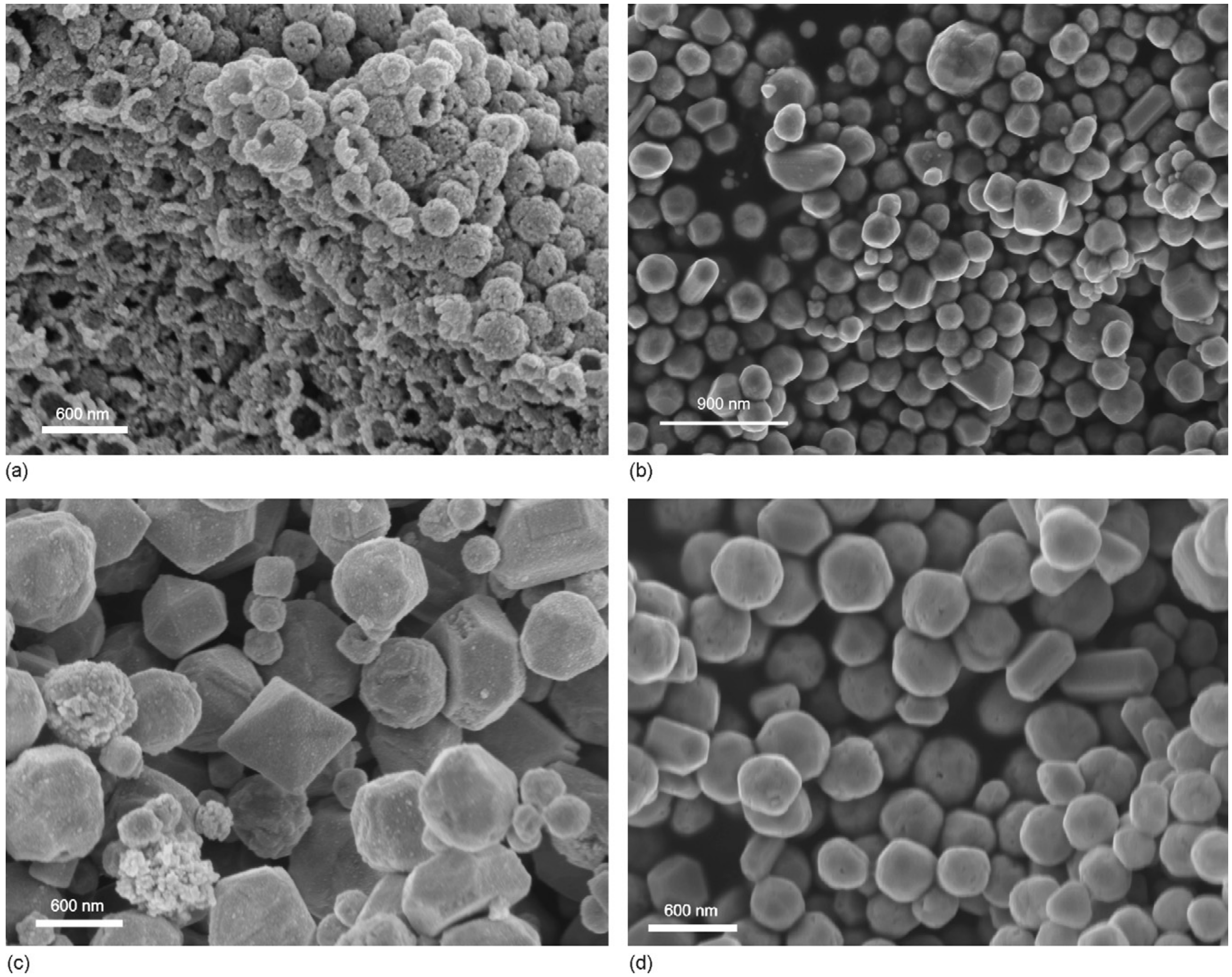

Fig. 4. SEM micrographs (magnification = 85,000×) of Cu(I) oxide and metallic Cu particles formed by the reduction of Cu(II) acetate in PD: (a) Exp 3D; (b) Exp 2E; (c) Exp 3F; (d) Exp 2I (explanation in the text, Table 1).

Cu_2O between 620 and 630 cm^{-1} (Fig. 2(B)). This observation suggests that PD is oxidized during the reduction process.[12,13] After 360 min, Cu_2O is reduced to metal copper as indicated by the absence of the absorption band at 630 cm^{-1} (Fig. 2(C)).

XRD diffractograms of the individual samples taken at different reaction times show the formation of Cu_2O at 175 °C after 85 min (Fig. 3(A), 2Θ peaks at: 36.4, 42.3, 61.6, 73.8), while only 15 min later intense characteristic signals of metallic copper and only very weak signals of Cu_2O were observed (Fig. 3(B)). The IR spectrum of the same sample (Fig. 2(B)) shows an intense band at 623 cm^{-1} indicating that Cu_2O is predominantly amorphous. The XRD of the final product after 360 min of reaction (Fig. 3(C)) shows the narrow, intense signals of metallic copper at 2Θ values: 43.4, 50.4 and 74.1. However, the IR spectrum (Fig. 2(C)) still shows a weak signal of Cu(I) oxide at this point, most probably due to copper oxidation on the surface of particles. Calculated crystallite sizes in prepared metallic Cu powders are in the range between 2 and 7 nm (Table 1) what is also clearly seen on SEM micrographs Figs. 1(b) and 4(c). This can be connected with the formation of particles, i.e. that larger particles are formed by the aggregation mechanism of small (nano-size) primary particles.[9]

SEM micrographs of Cu powders prepared at a $Cu(Ac)_2$ concentration of 0.01 mol/l show the formation of hollow particles with sizes between 100 and 300 nm consisting of smaller units of 20–50 nm (Fig. 4(a)). Since the particles are solid and of the same size at a $Cu(Ac)_2$ concentration of 1.0 mol/l (Fig. 4(b)) there might be some differences in the reaction or/and particle formation mechanisms. Namely, the mechanisms of precursor reduction in polyols and particle formation are still not fully elucidated. It is generally understood that precursors are dissolved by heating thus yielding ionic species which are then reduced to a metal. For the preparation of electrically conductive solids different mechanisms have been presented[9] suggesting that electrons from polyols can "hop" into the solid and reduce it even without complete dissolution.

In our case, complex mixtures with many by-products are formed during heating, indicating that both mechanisms are probably operating during the preparation procedure. PD is dehydrated during heating, thus producing different aldehydes which reduce the precursor to Cu_2O and then to metallic Cu, while the aldehydes themselves are oxidized to ketones or diketones.[9,14]

We presume that at different precursor concentrations the chemical reaction mechanism does not change but that there can be differences in the particle formation mechanism. The solubility product of intermediates at higher precursor concentrations in PD is certainly exceeded. It is possible that in such a case the undissolved intermediate particles are converted into metallic Cu by the migration of electrons between constituent subunits of the intermediate particles.[9]

In the final stage, after long reaction times, the size of the particles increases to 0.2–1 μm at a $Cu(Ac)_2$ concentration of 0.01 mol/l (Fig. 4(c)), while at 1.0 mol/l the average particle size of metallic Cu is 200–500 nm (Fig. 4(d)). This difference in particle size formed at 0.01 and 1 mol/l of $Cu(Ac)_2$ can be connected with the solubility of the precursor, which is completely dissolved at lower concentrations. Cu powders in both cases do not agglomerate. It is obvious from these preliminary results that Cu powders prepared in PD exhibit a wide range of particle sizes indicating that the conditions required to obtain monodisperse powders are not fulfilled.

Metallic Cu particles formed by the reduction of Cu(II) acetate in 1,2-propane diol have a smaller average particle size, a structure similar to particles prepared from $Cu(Ac)_2$ in glycerol,[7] and a particle size similar to those prepared in tetraethylene glycol.[9] Colloidal metallic Cu prepared from CuO in ethylene glycol without additives has a much higher particle size and the agglomeration is more intense[8] when compared to Cu particles prepared in PD.

4. Conclusions

Cuprous Cu(I) oxide and metallic Cu particles were prepared from Cu(II) acetate by reduction in 1,2-propane diol which is an environmentally friendly solvent. The resulting powders consist of non-agglomerated particles with average sizes between 100 nm and 1 μm. The formation of Cu(I) oxide takes place at temperatures between 150 and 170 °C. Amorphous cuprous oxide is further reduced to metallic Cu between 170 and 180 °C. The concentration of Cu(II) acetate precursor influences the mechanism of particle formation as well as the particle size and particle structure. Crystallite sizes in the prepared Cu powders are below 10 nm.

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