A Simple Way for Preparing Antioxidation Nano-copper Powders

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A two-step reduction route in polyol process for producing copper nano-particles with satisfied antioxidation property is described here. This process involves two-step reduction of copper salts in polyol solution with the surfactant protection under atmospheric conditions at a temperature below 353 K. Well-dispersed nano-copper particles with ca. 80 nm in diameter were obtained from the diethylene glycol (DEG) solution containing 0.2 M Cu^{2+} ion, 0.3 mM polyvinylpyrrolidone (PVP) as a ligand agent at 330 K, glucose as first reductant, and ascorbic acid as second reductant.

Nano-copper particles are intensely used currently in many fields because of their unique optical, electrical, and catalytic properties. Nanosized copper particles are currently sold for application in polymers and plastics, lubricants, inks, and metallic coatings. Nowadays, continued improvements in lithography have resulted in line widths that are less than one micron, thus classifying computer chips as an example of nanotechnology. The use of copper interconnects on silicon chips for use in personal computers is the first and most widespread use of copper in nanotechnology. It is this technology that has made it possible for personal computers to achieve speeds in the gigahertz range. Many techniques, such as mechanochemical method, atomizing method, electrolytic deposition method to cathode, ultrasonic electrolytic method, vaporization–deposition method, sol–gel method, wet reduction method, etc., have been reported to fabricate nano-copper particles.[1–6] However, copper powders obtained according to the above-mentioned method are most likely to have large variations in particle size and insufficient homogeneity, showing a lot of aggregation with poor antioxidaiton property. The oxidation of powders leads to the formation of a thick film conductor with bad appearance and poor solderability.

We report here the results on the synthesis and characterization of copper particles of specific size, shape, and narrow size distribution using a kind of new two-steps reduction method. This investigation was mainly undertaken two-steps reduction method for optimizing the reaction conditions required for producing antioxidation copper particles of nanoscale by reduction of copper salt in diethylene glycol (DEG), nucleation the metallic copper by homogeneous nucleation, growth of the nuclei and surface modification at the same process. Well-dispersed and antioxidation nano-copper particles with ca. 80 nm in diameter were obtained by this process.

This process involves adding DEG solutions of copper sulfate and an organic protective agent to a given volume of DEG under stirring. These materials were dissolved in DEG to form a polymer solution. Reactant solutions were mixed drop by drop with a burette. The first reduction agent was in stoichiometric excess of 2 times the copper sulfate to achieve complete reduction of the copper sulfate into cuprous oxide, and the second reduction agent was in stoichiometric excess of 1.5 times the cuprous oxide to achieve complete reduction of the cuprous oxide. The reaction solution was kept under agitation at a moderate speed to maintain the uniformity of the system and to keep the precipitated particles dispersed until the reduction was completed. Also, the dropping rate was sufficiently low to avoid foaming of the reaction dispersion. After 2 h of ageing, the precipitation was separated from the liquid solution by centrifugation and subsequently was washed with distilled water and alcohol for several times until a clear solution was obtained. The ultimate powders were then dried in a vacuum stove at 60 centigrade degree for 4 h.

Characterization of the metallic particles was achieved by different techniques. The X-ray diffraction patterns were obtained with an X-ray diffractometer (XRD; XRD-6000, Shimadzu Co., Japan) using Cu Kα radiation. The form and size of the final products were determined from microphotographs obtained with a scanning electron microscope (model S-700).

Figure 1 shows the XRD pattern, SEM image, and particle size distribution of a typical sample synthesized by reducing copper sulfate in DEG solution using this process. Figure 1a shows that all the peaks can be readily indexed to pure copper (JCPDS file No. 04-0836). The average grain size of the powder was calculated to be about 60 nm according to half width of the

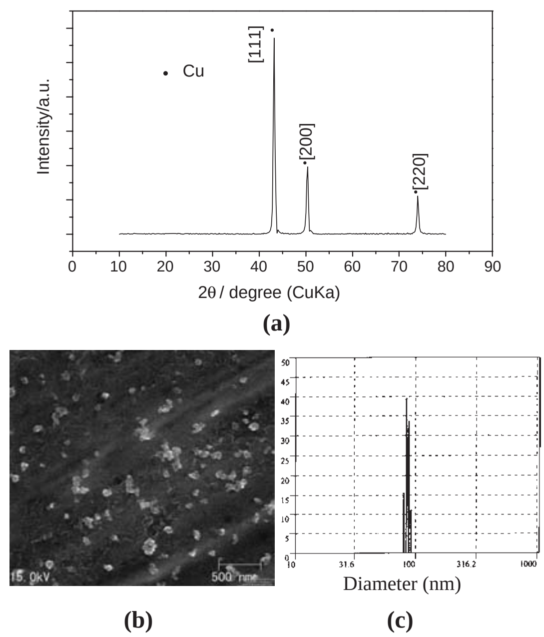


Figure 1. (a) XRD pattern of the as-synthesized copper particles (all peaks could be indexed to pure copper); (b) SEM image of as-synthesized copper particles; (c) Histogram of size distribution of as-synthesized particles.

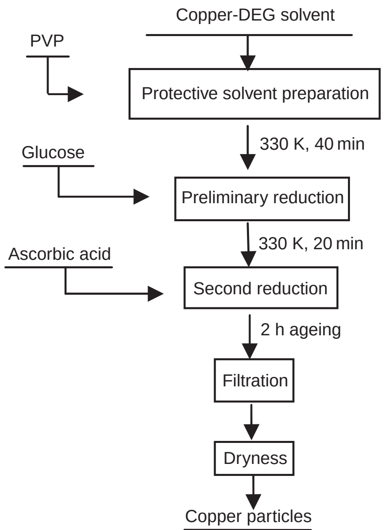


Figure 2. Sketch of process flow.

strongest diffraction peak using the Debye–Scherrer formula. Figure 1b shows the SEM image of a typical sample of the copper particles. The SEM image reveals that the product consists of spherical particles, and all nanoparticles are dispersed very well. The average diameter estimated from SEM image analysis is 70–80 nm. The size distribution is given by the histogram shown in Figure 1c, and one can clearly see that this powder has a narrow size distribution; the average diameter of these particles is estimated to be 85 nm, which is agreement with that analyzed by XRD and estimated by SEM. Thus, it can be concluded that this process gives uniform and well-dispersed copper nanoparticles.

Figure 2 shows the experiment process. This reaction scheme for producing copper powders using the polyol process involves two-step reduction of the soluble copper species in diethylene glycol, nucleation of Cu_2O and Cu, and growth of individual nuclei in the presence of a suitable protective agent. Mechanism of this process can be demonstrated by Figure 3. Upon fast addition of the diethylene glycol–copper sulfate solution to diethylene glycol-reductant ① solution, the soluble Cu(II) species are firstly reduced to Cu_2O (Figure 4). As the reaction process, the concentration of Cu_2O in solution increases, reaches the saturation concentration, then supersaturation, and finally the nucleation concentration. Spontaneous nucleation then takes place very rapidly, and many nuclei are formed in a short time, lowering the Cu_2O concentration below the nucleation and super-saturation levels into the saturation concentration region. The nuclei then grow by deposition of Cu_2O until the system reaches the saturation concentration. In the middle of the nuclei growth period, diethylene glycol-reductant ② is added into the solution, nearly all Cu_2O particles are compulsively stopped growing and be reduced into metallic Cu. All metallic Cu particles have grown at almost the same rate and the system exhibits a narrow size distribution (Figure 1) for the reason that all metallic Cu particles are reduced from uniform precursor: new generated Cu_2O nanoparticles. It can be seen that the two-step reduction not only disconnects nucleation and nucleation growth but also weakens conventional "eruptible nucleation" in this process. Therefore, particle–particle adhesion and agglomeration be prevented during the nucleation and growth steps. In traditional aggregation processes, particle coalescence is one of the main mechanisms by which the free energy of the system is lowered as a consequence of the decrease in interfacial area. Hindering particle coalescence is, therefore, very critical in the production of nano-metallic Cu powders by this process. Prevention of particle agglomeration and oxidation is achieved by adding a critical dosage of an organic protective agent whose function is to cover the particles, thus effectively eliminating any possibility of copper particle–copper particle bond formation. The presence of this agent at the solid/liquid interface, however, does not interfere with the copper diffusion–surface deposition process since the copper particles grow to a definite size.

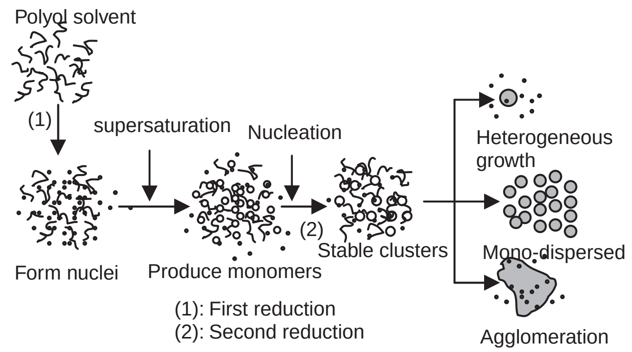
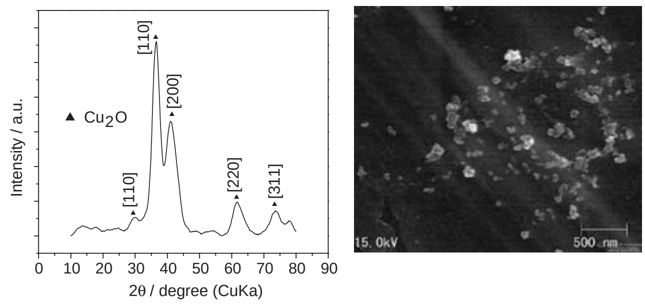


Figure 3. Demonstrative mechanism of two-step reduction route in polyol process.



(a) **(b)**

Figure 4. (a) XRD pattern of preliminary reduction product (all peaks could be indexed to Cu_2O); (b) SEM image of preliminary reduction product.

The two-step reduction method not only can compulsively disconnect nucleation and nucleation growth but also can weaken conventional eruptible nucleation. This process is convenient for delaying the nuclei process and for controlling copper particles morphology. Well-dispersed and antioxidation nano-copper particles with ca. 80 nm in diameter were obtained through two-step reduction in polyol process. This process successfully achieved nano-Cu particles fabrication and antioxidation at the same time.

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