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Preparation of Oleic Acid-capped Copper Nanoparticles

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A novel chemical process for producing hydrophobic nano-copper particles with satisfied antioxidation property is described here. Well-dispersed nano-copper particles with satisfied surface properties were obtained from the water/organic solution. In this process, oleic acid acts as both a phase-transfer agent and a particle protector coordinating their carboxyl end groups on the newly generated copper particles surface, and the hydrophobic carbon tails of the oleic acids are pointed outwards from the surface of particles. In addition, this organic film also plays an important role for preventing the newly generated copper particles from oxidation.

In contrast with noble metals such as Ag and Au, pure metallic copper particles usually cannot be obtained via the reduction of simple copper salts such as copper chloride or copper sulfate in aqueous solution, because the reduction tends to stop at the Cu_2O stage because of the presence of a large number of oxygenous water molecules, unless other reagents carrying functional groups that can form complexes with copper ions or soluble surfactants as capping agents to prepared copper particles in aqueous solutions are present. Despite zero valent copper initially forming in the solvent ultimately, it has been found that the zero valent copper can easily transform into oxides in those solvents with high dipole moments under ambient conditions.[1] Therefore, the traditional fabrication methods[2–5] were usually performed in nonaqueous media, at low precursor concentration, and under an inert atmosphere to avoid oxidation, which greatly hindered them be applied in mass-production.

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 extraction–two-step reduction method. In this method, Cu^{2+} ions in aqueous solution are firstly extracted into oleic acid. Then, the extracted Cu^{2+} ions are reduced into cuprous oxide and metallic copper by glucose and ascorbic acid, respectively. Oleic acid acts as both an extractant and a surfactant that can be adsorbed on the surface of the copper particles. Stable metallic copper particles can be obtained even in the presence of oxygen. This method enables us to obtain highly stable and hydrophobic nano-copper particles. Meanwhile, the presence of C=C bonds of oleic acid makes the final products easily react with polymer matrix, which is important for potential industrial process application.

Figure 1 shows the experiment procedure: in a typical experiment, two kinds of solutions were mixed firstly; one was aqueous 0.2 M $CuSO_4$ solution, while the other was 0.5 M oleic acid in ethanol/kerosene/acetone. Then, the mixed solution was shaken at normal condition for 30 min to attain the equilibrium of extraction. The copper ions extracted into the organic solvent were reduced by glucose and ascorbic acid solution, respectively. 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. 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 333 K for 4 h.

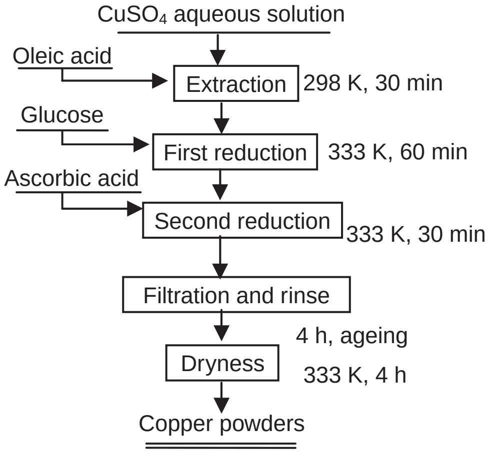

Figure 1. Flowchart.

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 morphology of the final products was determined from microphotographs obtained with a scanning electron microscope (model S-700). The effect of hydrophobic property was evaluated by the floating test: 5 g of the final sample was put into 50 mL of distilled water. We measured the ratio of floated product to overall weight of sample after they was mixed in distilled water and stirred vigorously. This ratio was called the active ratio. The higher the active ratio, the better the hydrophobic property was.

Figure 2 shows the XRD pattern, particles size distribution, and SEM images of a typical sample synthesized by reducing copper sulfate in extracted solution using this process.

It can be seen from Figure 2a 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 around 50 nm according to half width of the strongest diffraction peak using Debye–Scherrer formula. Figures 2c and 2d show the SEM

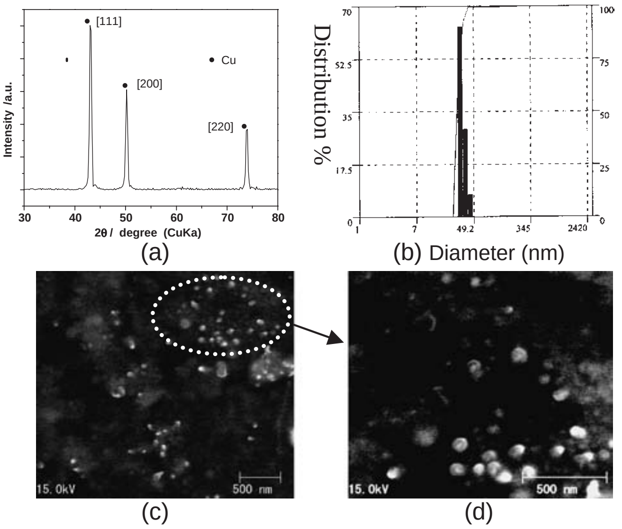

Figure 2. (a) XRD pattern of the as-prepared copper particles; (b) Histogram of size distribution of as-prepared particles; (c) and (d) SEM images of as-prepared copper particles.

images of a typical sample of the resultant copper particles. The SEM images reveal that the product consists of spherical particles, and all nanoparticles are dispersed very well. The average diameter estimated from SEM image analysis is 50–60 nm. The size distribution is given by the histogram shown in Figure 2b, and one can clearly see that this powder has a narrow size distribution; the average diameter of these particles is estimated to be 55 nm, which is agreement with that analyzed by XRD. Thus, it can be concluded that this process can produce uniform and well-dispersed copper nanoparticles.

Other experimental parameters being fixed, oleic acid content was changed to investigate the effects of the weight ratio of copper to oleic acid on the hydrophobic property of resultant copper particles.

Figure 3 shows the results of the hydrophobic property of resultant copper particles with different weight ratio of copper to oleic acid. From Figure 3 we can see, when the weight ratio of copper to oleic acid changes from 3.25 to 4.3 wt %, the resultant particles are hydrophobic. When this ratio changes from 32 to 65 wt %, all the resultant particles are hydrophilic. The hydrophobic property decreases step by step from 98.5 to 0.1% when the weight ratio of copper to oleic acid changes from 3.25 to 65 wt %. One can easily conclude that with the decreasing of the weight ratio to less than 3.25 wt %, the hydrophobic particle ratio will reach to nearly 100%. Therefore, we know that the optimum weight ratio of copper to oleic acid is around 3.25 wt %, because when the weight ratio of copper to oleic acid is more than 4.3 wt %, there are not enough hydrophobic functional groups from oleic acid to react with copper particles, and the most of copper particles are uncovered.

Oleic acid plays an important role throughout this process. It is firstly used as a phase-transfer agent, the Cu^{2+} ions in aqueous solution are first extracted into oleic acid/ethanol/kerosene/acetone. Then, the extracted metal ions are reduced into metal atoms by glucose and ascorbic acid. Because it has a high surface activity, the extractant, oleic acid, also acts as a surfactant to modify the newly generated particle surface coordinating their carboxyl end groups on the newly generated copper particle surface, the hydrophobic carbon tails of the oleic acids are pointed outwards from the surface of the particles.

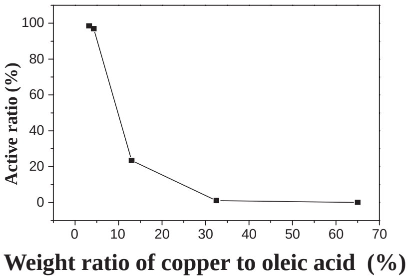

Figure 3. Effect of weight ratio of copper to oleic acid on particles' active ratio.

Oleic acid preventing the copper particles from oxidation is another role in this process, which occurs both during the growth step and the washing processes. For the former case, the steric effect arising from the long alkyl chain of oleic acid on the surface of copper particles may contribute to the antioxygen. Because the steric effect is largely determined by the covered fraction of oleic acid on the surface of the copper particles, it is, therefore, necessary that there is enough oleic acid to be adsorbed on copper particles. For the latter case, chemical bonding between the oleic acid and copper powders may play an important role in prohibiting oxidation of copper particles, because washing with water and alcohol several times did not completely remove the oleic acid from the surface of the copper particles, this point also can be induced from the hydrophobic experiment results. These experiments imply that the steric effect also exists during the washing process. By which, this fabrication method realizes preparation of nano-copper particles and antioxidation in one process.

Well-dispersed and antioxidation nano-copper particles with ca. 50 nm in diameter were obtained through the extraction–two-stepreduction process. This process successfully achieved nano-Cu particles fabrication, antioxidation, and hydrophobic property at the same time. Oleic acid preventing the copper particles from aggregation is the one role of this surfactant, while preventing the copper particles from oxidation is another role. Furthermore, the existence of the oleic acid-capping layer effectively prevented the surface from adsorbing water around the resultant nanoparticles, which made the resultant particles possess excellent hydrophobic property.

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