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A new method for preparing hydrophobic nano-copper powders

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Abstract A novel chemical process for producing hydrophobic nano-copper particles with satisfied anti-oxidation property is described here. The resultant particles have been characterized by X-ray diffraction, size distribution analysis and SEM, TEM observation. Well-dispersed nano-copper particles with c.a. 30 nm in diameter were obtained from the water/organic solution containing 0.2M Cu^{2+} ion, glucose as the first reductant, ascorbic acid as the second reductant. In this process, oleic acid acted as both a phase-transfer agent and a particle protector coordinating their carboxyl end groups on the new generated copper particles surface, the hydrophobic carbon tails of the oleic acids were pointed outwards from the surface of the synthesized particles. This organic film seems to play an important role for prevent the new generated copper particles from oxidation. In addition, this process also adopting two-step reduction method can lead compulsively disconnect nucleation and nucleation growth, and weaken conventional eruptible nucleation. By controlling the first reduction product's size, this process is more convenient for delaying the nuclei processes and for controlling the ultimate copper particles size.

Introduction

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 due to the presence of a large number of oxygenous water molecules, unless other reagents carrying functional groups that can form complexes with copper ions are present or using soluble surfactants as capping agents to prepare copper particles in aqueous solutions. However, 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 [2–8] were usually performed in non-aqueous media, at low precursor concentration, and under an inert atmosphere to avoid oxidation, which greatly hinder 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, cupric ions in aqueous solution are firstly extracted into oleic acid. Then, the extracted cupric 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 adsorb on the surface of the copper particles. Stable metallic copper particles can be obtained

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even in the presence of air 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.

Experimental

Materials

All chemicals used were reagent grade. Copper sulfate, glucose, ascorbic acid, oleic acid, ammonia and H_3PO_4 were purchased from Japan Nacalai teceque Inc. Ammonia and H_3PO_4 were used to adjust the pH value, without further purification.

Procedure

Figure 1 shows the experiment procedure: in a typical experiment, two kinds of solutions were mixed first; one was aqueous solution 0.2M $CuSO_4$, while the other was 0.5M 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. 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. 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 the vacuum stove at 60 °C for 4 h.

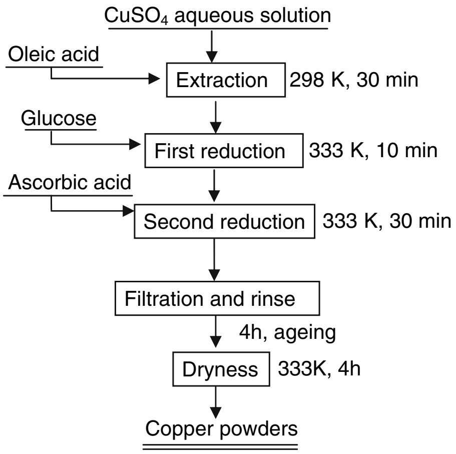


Fig. 1 Sketch of process flow

Characterization of the metallic particles was achieved through different techniques. The X-ray diffraction patterns were obtained with an X-ray diffractometer (XRD; XRD-6000, Shimadzu Co., Japan) using CuKa radiation. The morphology of the final products was determined from microphotographs obtained with a transmission electron microscope (JEOL-TEM). 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.

Results and discussion

Particle size and structure

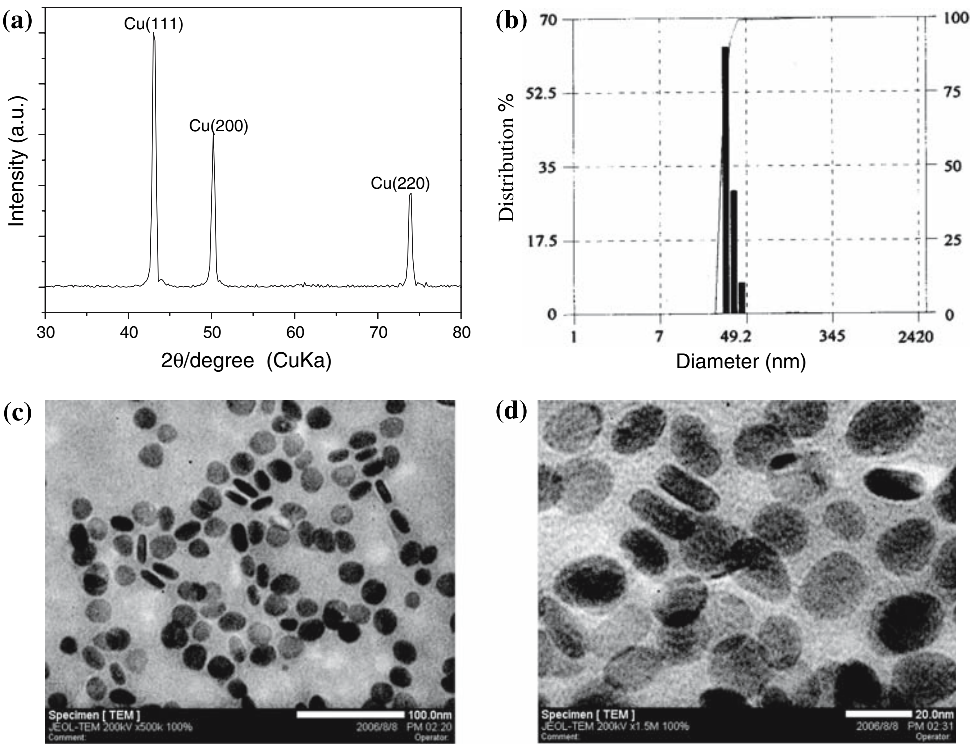
Figure 2 shows the XRD pattern, particles size distribution and TEM images of a typical sample synthesized by reducing copper sulfate in extracted solution using this process.

It can be seen from Fig. 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 20 nm according to half width of the strongest diffraction peak using Debye-Scherrer formula. Figure 2c, d shows the TEM images of a typical sample of the copper particles. The TEM images reveal that the product consists of spherical particles, and all nanoparticles are dispersed very well. The average diameter estimated from TEM images analysis is 20–30 nm. The size distribution is given by the histogram shown in Fig. 2b, and one can clearly see that this powder has a narrow size distribution; the average diameter of these particles is estimated to be 45 nm, which is agreement with that analyzed by XRD and estimated by TEM. Thus, it can be concluded that this process gives uniform and well-dispersed copper nano-particles.

Hydrophobic property

Varied oleic acid quantity and fixed the others experiment parameters to explore the effects of the weight ratio of copper to oleic acid on the hydrophobic property of resultant copper particles.

Fig. 2 XRD pattern, particles size distribution and TEM images of a typical sample



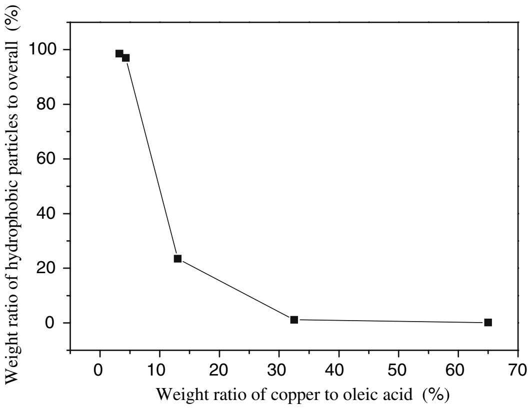


Fig. 3 Effect of the weight ratio of copper to oleic acid on the hydrophobic property of resultant copper particles

Figure 3 shows the results of the hydrophobic property of resultant copper particles with different weight ratio of copper to oleic acid. From Fig. 3 we can see, when the weight ratio of copper to oleic acid changed from 3.25 to 4.3 wt%, the resultant particles were hydrophobic. When the weight ratio changed from 32 to 65 wt%, all the resultant particles were hydrophilic. The hydrophobic property decreased step by step from 98.5 to 0.1% when the weight ratio of copper to oleic acid changed 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 property particles ratio will reach to nearly 100%. Therefore, we knew 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 were no enough hydrophobic function groups from oleic acid to react with copper particles, and the most of copper particles was uncovered.

Mechanism of this process

Mechanism of this process can be demonstrated by Fig. 4. Upon fast addition of the reductant (1) solution into the extracted solution, the extracted soluble Cu(II)-oleic acid species are firstly reduced to Cu_2O (Fig. 5). As the reaction process, the concentration of Cu_2O in solution increase, reaches the saturation concentration, then super-saturation 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. At the end of the nuclei growth period, reductant (2) solution 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 thus the system exhibits satisfied morphology property (Fig. 2) for the reason that all metallic Cu particles are reduced from uniform precursor: new generated Cu_2O nano-particles [8].

Fig. 4 Schematic illustration for the mechanism of this process

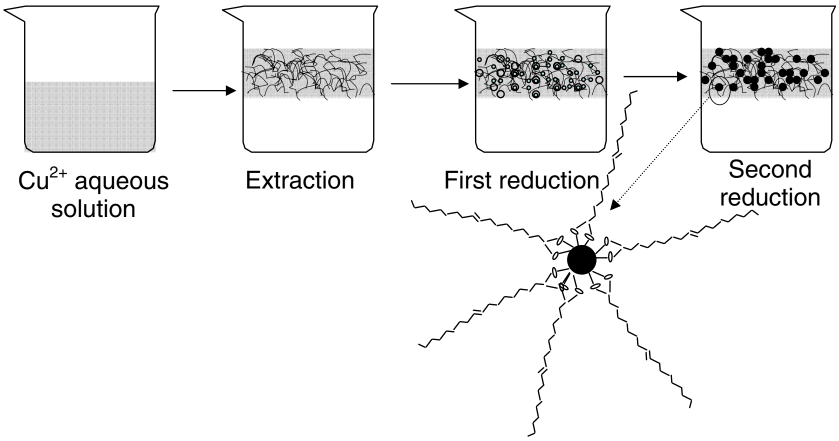
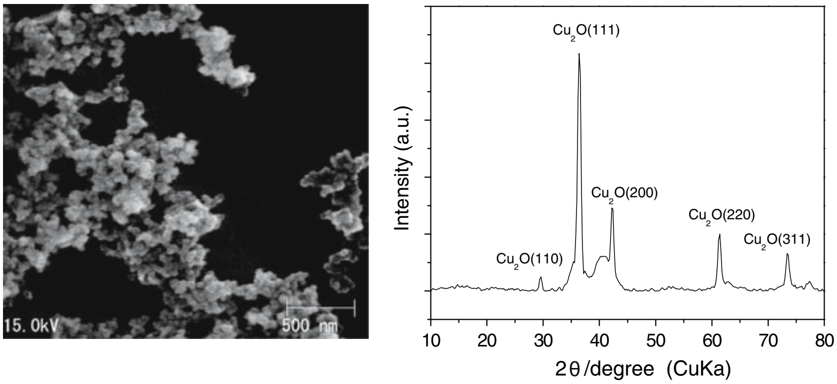


Fig. 5 SEM image and XRD pattern of the first reduction product



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 respectively. Because it has a high surface activity, the extractant oleic acid also acts as a surfactant to modify the new generated particles surface coordinating their carboxyl end groups on the new generated copper particles surface, the hydrophobic carbon tails of the oleic acids were pointed outwards from the surface of the synthesized particles. Oleic acid's function in this process was generally proposed on the basis of the following reactions.

$$2C_{17}H_{33}COOH + Cu^{2+} \rightarrow Cu(C_{17}H_{33}COO)_2 + 2H^+ \qquad (1)$$

$$2Cu(C_{17}H_{33}COO)_2 + C_6H_{12}O_6 + 5OH^- \rightarrow Cu_2O + C_5H_{11}O_5COO^- + 4C_{17}H_{33}COO^- + 3H_2O \qquad (2)$$

$$Cu_2O + C_6H_8O_6 + 2n\ C_{17}H_{33}COOH \rightarrow 2Cu(C_{17}H_{33}COOH)_n + C_6H_6O_6 + H_2O \qquad (3)$$

Oleic acid preventing the copper particles from aggregation and making the resultant copper particles with hydrophobic property are the two main roles of this surfactant, while it 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 anti-oxygen. Because the steric effect is largely determined by the covered fraction of oleic acid on the surface of the copper particles, it was, therefore, necessary that there be enough oleic acid to adsorb 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 implied that the steric effect also exists during the washing process. By which, this fabrication method is realized to prepare nano-copper particles and anti-oxidation in one process.

Conclusions

Well-dispersed and anti-oxidation nano-copper particles with c.a. 30 nm in diameter were obtained through the Extraction-two step-reduction process. This process successfully achieved nano-Cu particles fabrication, anti-oxidation and hydrophobic property at the same time. This method not only can compulsively disconnect nucleation and nucleation growth, but also can weaken conventional eruptible nucleation, which is convenient for delaying the nuclei process and for controlling copper particles morphology. Oleic acid preventing the copper particles from aggregation is the one role of this surfactant, while it preventing the copper particles form oxidation is another role. Furthermore, the existence of the oleic acid-capping layer effectively prevented the surface adsorbed water around the resultant nanoparticles, which made the resultant particles possess excellent hydrophobic property.

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References

1. Xinyu S, Sixiu S, Weimin Zh, Zhilei Y (2004) J Colloid Interface Sci 273(2):463
2. Amit S, Sharma BP (2002) Mater Res Bull 37:407
3. Bin Z, Zhijie L, Zongtao Z, et al. (1997) J Solid State Chem 130:157
4. Ding J (1996) J Alloys Comp 234:L1
5. Xuan-hui Q, Boyun H, Changming L et al. (1995) J Central South Univ Technol 26(6):781
6. Kazushi S, Yoshihiro O, Hiromasa M, US Patent, 6,881,240
7. Xie-bin Z, Xue-chen D (2004) ShangHai Nonferrous Metals 25(3):97
8. Jian-guang Y, Okamoto T, Ichino R, Bessho T et al (2006) Chem Lett 35(6):648