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Copper nanoparticles were successfully synthesized by 60Co-γ radiation with aqueous solution of cupric sulfate under inert nitrogen-purged conditions. Cu nanoparticles were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), laser particle size distribution analyzer (LSPSDA) and differential scanning calorimeter (DSC) techniques, respectively. The effects of solution system, pH, additive of surfactant and absorbed doses on the particle size and its distribution as well as stored stability of Cu naoparticles were investigated. High resolution TEM pictures showed the formation of homogeneous cubic-structured copper nanoparticles with different sizes depends on the synthetic conditions. This new kind of synthesis method shows the excellent stability, which may provide an efficient way to improve the fine tuning of the structure and size of copper nanoparticles.

Full Text

Preamble

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Preparation of Copper Nanoparticles by Radiation

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Abstract

Copper nanoparticles were successfully synthesized via ^{60}Co-γ radiation in an aqueous solution of cupric sulfate under inert nitrogen-purged conditions. The Cu nanoparticles were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), laser particle size distribution analyzer (LSPSDA), and differential scanning calorimetry (DSC) techniques. The effects of solution system, pH, surfactant additives, and absorbed doses on particle size, size distribution, and storage stability of Cu nanoparticles were investigated. High-resolution TEM images demonstrated the formation of homogeneous cubic-structured copper nanoparticles with varying sizes depending on synthetic conditions. This novel synthesis method exhibits excellent stability and may provide an efficient approach for fine-tuning the structure and size of copper nanoparticles.

Key words: ^{60}Co-γ radiation, Copper nanoparticle, Characterization

Introduction

Due to the unique properties of metallic copper, such as interesting optical, electronic, magnetic, and chemical characteristics, Cu nanoparticles are widely used in lubrication additives, conductive pastes, information storage, effective antibacterial agents, catalysts, photoelectric devices, and other fields. The synthesis of copper nanoparticles can be performed through physical vapor deposition, electrochemical deposition, decomposition of organometallic compounds, liquid-phase reduction, hydrothermal methods, microemulsion techniques, and so on.

A burst of research activity has been reported in the synthesis and fabrication of Cu nanoparticles with different sizes and shapes. However, developing a reproducible method for synthesizing copper nanoparticles with a specific size, well-defined surface composition, and long storage stability remains a challenging task. Very little work has been carried out on room-temperature synthesis of copper nanoparticles. We have attempted to synthesize size-controlled copper nanoparticles through a simple aqueous system using ^{60}Co-γ radiation.

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2.1 Materials

$CuSO_4 \cdot 5H_2O$, AR, from Wenzhou Chemical Co. Ltd.
Isopropyl alcohol (IPA), AR, from Shuanglin Chemical Co. Ltd. of Hangzhou.
Absolute ethyl alcohol, AR, from Damao Chemical Co. Ltd. of Tianjin.
Polyvinyl alcohol (dynamic viscosity 54.0-66.0 $mPa \cdot s^{-1}$), AR, from National Chemical Co. Ltd.
25% aqueous ammonia, CP, from Dafang Chemical Co. Ltd. of Hangzhou.
Acetic amine, AR, from Hewei Chemical Co. Ltd. of Shanghai.

Dodecyl mercaptan, CP, from Shanghai Chemical Co. Ltd. of National Medicine Company.
Sodium dodecyl benzenesulfonate (SDBS), CP, from Guanghua Chemical Co. Ltd. of Shantou.
NNHDA, dodecyl alcohol amine, CP, from Yinghu Chemical Co. Ltd. of Hangzhou.
Sodium carboxymethyl cellulose, CP, from Chemical Co. Ltd. of National Medicine Company.
Oleamide, CP, from Shentong Chemical Co. Ltd. of Zibo.
Oleic acid, CP, from Shuanglin Chemical Co. Ltd. of Hangzhou.

2.2 Facility and Instruments

Irradiation was performed using a 10^5 Curie ^{60}Co-γ source at the Irradiation Center Facility of Zhejiang University. The crystal phase was determined using X'Pert Pro (XRD, Cu Kα λ=1.541 Å). Morphology and particle size were measured using a JEM-1230 transmission electron microscope (TEM). Particle size and distribution were measured using a Nano ZS-90 (LSPSDA), and the melting point of Cu particles was determined using an SDT Q600 (DSC). Additional equipment included a KQ-50DA ultrasonic disperser, TG20M centrifuge, DZF-6050 vacuum oven, and 85-2 magnetic stirrer for sample treatment.

2.3 Sample Preparation Process

A specified amount of surfactant (PCM) aqueous solution was added to the $CuSO_4$ aqueous solution under stirring conditions, followed by the addition of isopropyl alcohol as a scavenger for OH• radicals produced from water radiolysis. The pH of the solution for irradiation was adjusted to 6.5 using NH_4OH-NH_4Ac and deoxygenated by bubbling with N_2 for 30 minutes. The irradiation for preparing Cu nanoparticles was performed using a 10^5 Curie ^{60}Co-γ source with different absorbed doses. The solution color changed from blue to purplish red after irradiation.

The sample was washed with absolute ethyl alcohol free from O_2, dried at 60°C and −0.01 Pa, and stored in a small reagent bottle filled with high-purity N_2 for further characterization.

The reduction of copper cations can be described as follows:

$$H_2O \rightarrow[\gamma\text{-rays}]\ e\,q^-,\ H\cdot,\ OH\cdot,\ H_3O^+,\ H_2,\ H_2O_2$$
$$Cu^{2+} + e\,q^- \rightarrow Cu^+$$
$$OH\cdot + \text{iso-PrOH} \rightarrow \text{iso-PrO}\cdot + H_2O \qquad (2)$$
$$Cu^+ + e\,q^-\ (H\cdot,\ \text{iso-PrO}\cdot) \rightarrow Cu^0$$
$$nCu^0 \rightarrow Cu\ \ \text{(crystal)}$$

The radiolytic products of water, such as e q^- and H•, can effectively reduce copper cations, while the iso-PrO• formed from scavenging of OH• by isopropyl alcohol can also reduce them. Some Cu atoms accumulate to form a crystal and grow into a nanoparticle.

3.1 Effect of Surfactants on Properties and Size of Cu Nanoparticles

To achieve good dispersity and stability of Cu atoms formed in the irradiated solution, different surfactants were used in the preparation solution, including polyvinyl alcohol, sodium dodecyl benzenesulfonate, polypropylene pyrrolidone, polyacrylamide, Tween 80, sodium alginate, and PCM. The preparation conditions were: 1.0 g/100 mL surfactant, 0.05 mmol $\cdot$ L^{-1} $CuSO_4$, 2 mol $\cdot$ L^{-1} IPA, pH adjusted by NH_4OH/NH_4Ac for irradiation. The results are listed in Table 1 .

The supernatant of the irradiated sample was removed after centrifugal separation, and a deactivation agent was added to the remaining solution to prevent oxidation of the Cu nanoparticles. After several alternating washes with deionized water and absolute ethyl alcohol, the sample was dried at 60°C and −0.01 Pa.

Table 1. Results of samples with different surfactant additives obtained after irradiation with absorbed doses of 100 kGy

Sample	Surfactant	Aspect of solution
1	Polyvinyl alcohol	Purplish red
2	Sodium dodecyl benzenesulfonate	Purplish red
3	Polypropylene pyrrolidone	Purplish red
4	Polyacrylamide	Black bulk sediment
5	Tween 80	Black sediment
6	Sodium alginate	Black sediment
7	PCM	Purplish red, stable

The solution color was blue with all different surfactant additives before irradiation. In samples 1, 2, and 3, Cu^{2+} could be reduced to form purplish red Cu nanoparticles under radiation. However, the solution turned black within 20 minutes after irradiation, indicating that reduced Cu was oxidized to Cu_2O in air. In samples 4, 5, and 6, the solution appeared black with black sediment observed immediately after irradiation, suggesting these three surfactants could not protect reduced Cu from oxidation during the radiation process, and the particles might be composed of Cu_2O or Cu_2O+Cu. In contrast, using the PCM surfactant system developed by our group, purplish red Cu nanoparticles with excellent stability were obtained, as the PCM surfactant residues contained both carboxyl and amide groups, which provided good distribution and oxidation protection for the Cu nanoparticles. Therefore, PCM surfactant was used for all subsequent Cu nanoparticle preparations in this study.

The effect of different surfactant concentrations on Cu nanoparticle size was investigated using LSPSDA and TEM characterization. As shown in Figs. 1 and 2 [Figure 1: see original paper][Figure 2: see original paper], the particle sizes and distributions decreased with increasing PCM concentration, and the samples showed circular morphology with good distribution. The average particle size was 122.4 nm at a PCM concentration of 0.6 g/100 mL, and decreased to 21.3 nm at 2.2 g/100 mL. This suggests that PCM adsorbed on the Cu nanoparticle surface may form an electric double layer, which stabilizes the particles in solution or air and protects them from oxidation.

3.2 Relationship Between Size and Melting Point of Cu Nanoparticles

Generally, the melting point of a material is defined as the temperature at which equilibrium between solid and liquid phases occurs for a pure material at fixed pressure, with the phase transition free energy change following $\Delta G=0$. For solid pure materials with high degrees of dispersion, such as nanoparticles, chemical potential must be related to particle size, even though potential is a function of both pressure and temperature. Therefore, the melting point of Cu nanoparticles with different sizes can be used to describe their properties.

DSC was used to determine the melting points of Cu nanoparticles with particle sizes of 122.4 nm, 91.2 nm, 58.9 nm, 28.0 nm, and 21.3 nm, respectively. The results are shown in Fig. 3 [Figure 3: see original paper].

As shown in Fig. 3, the melting point of Cu nanoparticles decreases with decreasing particle size. The melting point is 439.71°C for 122.4 nm particles, and 139.9°C for 21.3 nm particles, which is significantly lower than the 1083.4°C melting point of bulk copper.

3.3 Effect of pH on the Phase of Cu Nanoparticles

The chemical properties of Cu nanoparticles are very active, as $E^0(Cu^{2+}/Cu) = 0.337$ V. This means some Cu_2O may exist in Cu nanoparticles formed from Cu^{2+} reduction in solution induced by γ-rays. The pH of the solution may play an important role in the reduction process. XRD was used to determine the phase of Cu nanoparticles obtained at pH values of 3.6, 5.1, 6.5, 7.2, and 9.5, respectively.

As shown in Fig. 4 [Figure 4: see original paper], the X-ray diffraction angles (2) for samples a, b, c, and d are 43.53°, 50.24°, 74.91°, and 89.88°, which match well with the standard XRD angles for Cu listed in card 01-085-1326 as characteristic parameters. This indicates that Cu nanoparticles formed at these pH values are composed of pure Cu. When the solution pH was 7.2 and 9.5, besides the diffraction angles for pure Cu, additional peaks at 2 = 36.35° and 61.36° were observed, corresponding to the characteristic XRD angles of Cu_2O listed in card 00-005-0667, confirming that Cu_2O formed. The amount of Cu_2O

increased with increasing pH value. No characteristic XRD peaks of CuO were observed in our study.

3.4 Effect of Absorbed Doses on the Formation of Cu Nanoparticles

As shown in Fig. 5(a) [Figure 5: see original paper], the supernatant of the irradiated sample with an absorbed dose of 50 kGy remained blue after centrifugal separation, indicating that some Cu^{2+} had not been completely reduced. However, Cu nanoparticles with good distribution and small particle size formed, though some incomplete particles were observed. At 150 kGy, the supernatant color became transparent from the amaranth of the irradiated sample after centrifugation, and the obtained Cu nanoparticles showed good distribution with small size, as shown in Fig. 5(b). However, as shown in Fig. 5(c), some aggregation was observed in Cu nanoparticles from the sample irradiated with 300 kGy, and the particle size became larger even though Cu^{2+} was completely reduced. At 500 kGy (Fig. 5(d)), serious aggregation occurred in the Cu nanoparticles. This suggests that the surface electric charge of Cu nanoparticles modified by surfactant may be lost due to radiolytic decomposition of surfactants at higher absorbed doses.

3.5 Effect of Deactivation on Storage Performance of Cu Nanoparticles

Metallic nanoparticles can be easily oxidized in air, so Cu nanoparticles were deactivated using six compounds: NNHDA, dodecyl mercaptan, $\{C_{11}H_{23}CON(CH_2CH_2OH)_2\}$, stearic acid, oleic acid, oleamide, and castor oil. The deactivated samples were stored in air or alcohol, and the Cu_2O diffraction peak was detected by XRD to identify whether Cu nanoparticles were oxidized at different storage times.

In Fig. 6 [Figure 6: see original paper], for samples without any deactivation treatment stored in air (a) or alcohol (b) for 5 days, characteristic diffraction peaks at 2 = 36.40° and 61.3° were observed, with higher peaks in air than in alcohol, indicating that some Cu nanoparticles were oxidized to Cu_2O, especially in air. Samples deactivated by stearic acid (c), oleic acid (d), oleamide (e), castor oil (f), and NNHDA (g) also showed oxidation, though NNHDA showed weaker oxidation compared to others. Only the sample deactivated by dodecyl mercaptan (h) showed no characteristic Cu_2O diffraction peaks, displaying only those of pure Cu (2 = 43.35°, 50.49°, 74.11°, and 89.88°).

When the storage time was extended to 42 days in alcohol (Fig. 7 [Figure 7: see original paper]), the characteristic Cu_2O diffraction peaks in the sample deactivated by NNHDA disappeared, possibly due to reduction of Cu_2O by active H • in the NNHDA molecule. However, samples deactivated by stearic acid, oleic acid, oleamide, and castor oil remained oxidized, except for the dodecyl mercaptan sample.

Since both NNHDA and dodecyl mercaptan could effectively protect Cu nanoparticles from oxidation, prepared Cu nanoparticles were stored in NNHDA and dodecyl mercaptan for 140 days. XRD determination showed no characteristic Cu_2O diffraction peaks, only those of pure Cu, as shown in Fig. 7. This indicates both compounds can effectively protect Cu nanoparticles. Compared with dodecyl mercaptan, NNHDA is water-soluble, non-toxic, and cheaper, making it the preferred choice for protecting Cu nanoparticles from oxidation for further study and application.

4 Conclusion

Cu nanoparticles can be prepared by irradiating $CuSO_4$ aqueous solution at room temperature without additives. XRD, TEM, and DSC characterization revealed that the amaranth-colored Cu nanoparticles with particle size less than 100 nm and melting point of 139.90°C are globular powders of pure copper.

The PCM surfactant added to the reaction system enables good dispersity of Cu nanoparticles, with particle size decreasing as PCM concentration increases, providing a method to control particle size and distribution.

The effect of reaction system pH on Cu nanoparticle formation was investigated. Cu nanoparticle preparation should be performed in the pH range of 4.0–6.5, as Cu_2O forms when $pH > 7.2$ and Cu^{2+} reduction cannot be completed when $pH < 4$.

The optimal absorbed doses for preparing Cu nanoparticles are in the range of 150–250 kGy.

NNHDA, as a deactivation agent, can protect Cu nanoparticles from oxidation even after storage for more than 140 days. The productivity of Cu nanoparticles is 89%.

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