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Preparation of copper nano-particle powder by γ-irradiation

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Abstract Copper nano-particles were prepared by 100 kGy room temperature γ-ray irradiation of $CuSO_4$ aqueous solution added with surfactant and inactive agent. Effects of the surfactants and pH value on particle size and morphology of the Cu powder, and the storage stability, were investigated. Structure, morphology, particle size and melting point of the copper nano-particles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), laser particle size analyzer and differential scanning calorimetry (DSC), respectively. The results show that the Cu nano-particles prepared with PCM as surfactant and N, N-bis-hydroxyethyl dodecyl amide as inactive agent, in pH=4.0–6.5 of the aqueous solution, can be stored in air for 140 days.

Key words γ-rays irradiation, Nano-copper, Characterization

1 Introduction

Nanomaterials have been a hot topic of chemistry, physics and materials science in recent years, due to their unique mechanical, electrical, magnetic, thermal and chemical performances. A wide variety of nanoparticles has been prepared by physical methods including evaporation, ultrasonic fragmentation, explosion etc., and by chemical methods such as carbonylation, gas-state reaction, gas reduction, aqueous solution reduction, precipitation and spray. The application of physical method is sometimes restricted by the big cost on the equipments, while the chemical methods to prepare nano-powder are used specially in laboratories. As a new method, γ-ray irradiation has been used to prepare nanoparticles of metal, alloy and oxides[1-3]. Metal ions in a solution can be reduced by hydrated electrons produced from the irradiated water to form nanoparticles *via* reunion process of reduced species. When aqueous solution is irradiated by gamma ray, water molecules undergo a radiolysis process that produced radiolysis products. Elemental processes for the reduction of noble metal ions by γ-rays lead to the formation of metal monolithic nanoparticles as follows:

$$H_2O\rightarrow H_2,\ H_2O_2,\ H_2O^{\cdot},OH,e_{aq}^{-},\ H_2^{+}O \qquad (1)$$

$$Cu^{+}\rightarrow Cu^{2+}+e_{aq}^{-} \qquad (2)$$

$$n\mathrm{Cu}^{0}\rightarrow \mathrm{Cu}_{n} \qquad (3)$$

Radical H· and e^{-}_{aq} are well known as strong reducing agent, with standard reduction potentials of respectively –277 V and –213 V, hence the reduction of metal ions in aqueous solution to metallic state. Adding isopropanol to the solution helps to eliminate oxyradical $^{\cdot}OH$, and the radical $H^{\cdot}$ and e_{aq}^{-} in the aqueous solution reduce metal ions to lower valence and finally to metallic state. Their nucleation leads to nanoparticle precipitates from the solution[5]. Nano copper powder in average particle size of about 50 nm could be obtained by γ-ray irradiation combined with hydrothermal crystallization[6].

We developed a new preparation process to prepare metal nanomaterials of well controlled particles size, using γ-ray irradiation[7–9], without any catalysts and chemical initiators. In this work, copper nanoparticles were synthesized in aqueous solution using gamma irradiation. Influencing factors of the particle size in different experimental conditions were investigated.

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2 Materials and methods

2.1 Chemical reagents

Copper sulphate ($CuSO_4·5H_2O$, AR), isopropanol (IPA, AR), ethanol, polyvinyl alcohol (viscosity at 54.0–66.0,CP), 25% ammonia (AR), acetamide (AR), dodecanethiol (CP), sodium dodecyl sulfate (SDBS, CP), N,N-bis-hydroxyethyl lauryl amide and amine association complexes (CP), sodium carboxymethyl cellulose (CP), oleamide (CP), oleic acid (CP) were used in the experiment.

2.2 Equipments

X'PertPRO X-ray diffraction (XRD, Cu Kα, λ=1.54178 Å), NaNo ZS-90 laser diffraction particle size distribution analyzer, SDT Q600 differential scanning calorimeter (DSC), JEM-1230 transmission electron microscope (TEM), KQ-the 50DA ultrasonic cleaner, TG20M high-speed centrifuge, DZF-6050 vacuum oven, and 85-2 magnetic blender. The sample solutions were irradiated to 100 kGy in a ^{60}Co γ-ray source of 2.96×10^{15} Bq.

2.3 Solution preparation and irradiation

The concentration of copper sulfate and isopropanol in aqueous solution was 0.05 and 2.0 mol/L, respectively, added with different kinds of surfactants PCM (Phase Change Materials, prepared in our lab) in 2.2 g/100 mL (2.2 wt%). A certain amount of $CuSO_4·5H_2O$ was dissolved in an appropriate amount of deionized water using a stirrer. Under stirring of the solution, the surfactant solution was added slowly, and then a certain amount of isopropyl alcohol (IPA) was added as inactive agent. After adjusting the pH to 6.5 using buffer of NH_3-H_2O/NH_4Ac, the solutions were transferred into containers, bubbled with nitrogen to remove oxygen, and irradiated to 100 kGy.

2.4 Collection of the nano-particles

The irradiated solution was centrifuged to remove the supernatant. The passive agent was added immediately to inactivate the particle surface. Then deionized water/ethanol mixture free from oxygen was used to wash and centrifuge the sample for tree times. The samples were vacuum-dried at below 60°C for 12 h. The prepared samples were stored for characterization.

2.5 Characterization of the nano-particles

Phase analysis of the stored Cu nanoparticles, or those collected directly from centrifuging and drying process was performed by XRD. The samples for measurements of the particle size and size distribution were prepared as follows: fresh copper nanoparticles were washed with alcohol and distilled water for several times, and dissolved in anhydrous ethanol. After dispersion by use of ultrasonic vibration, the particle sizes were determined by the NaNo-ZS-90 laser diffraction particle size distribution meter. Morphology of the nanoparticles was observed by the TEM with the sample dissolved in anhydrous ethanol and dispersed by ultrasonic vibration for 5 min.

3 Results and discussion

3.1 Selection of surfactants

In studying the surfactant effect on the formation of Cu nanoparticles in irradiation process, concentration of $CuSO_4$ aqueous solution was kept at 0.05 mol/L, and the additive concentration of IPA as OH radical scavenger was 2.0 mol/L. Seven kinds of surfactants were added in reaction system at concentration of 2.2% (wt.%). The aqueous solution for irradiation was adjusted to pH6.5 by use of NH_3-H_2O/NH_4Ac. After irradiating the N_2-bubbled solutions to 100 kGy, the changes in color are listed in Table 1.

Table 1 Changes in color of the solutions with different surfactants, irradiated to 100 kGy.

Surfactant	Solution status
Polyvinyl alcohol (PVA)	Purple
Sodium dodecyl benzene sulfonate	Purple
Polyacrylamide(PAM)	Black massive precipitation
Tween 80	Reddish black precipitate
Sodium alginate	Bluish black precipitate
Polypropylene pyrrolidone	Purple
PCM	Purple, stable

Black precipitates occur in the solutions with Tween 80 and sodium alginate. They cannot protect the copper particles formed in the irradiation process.

According the color of particles, it is possible that the Cu^{2+} will be reduced by e_{aq}^- produced from radiolysis of water to form Cu or Cu^+, so the products of Cu_2O or Cu^+. The Cu_2O with black or reddish black color may come from oxidation of reduced Cu without protection by the surfactant. Purple color were observed in other irradiated samples, indicating that Cu^{2+} was reduced to Cu and gathered into nanoparticles[10]. Especially, the sample of PCM kept the purple color even stored over night in air. And existence of carboxyl and amide groups in sample was confirmed by IR spectroscopy. Then, the PCM surfactant protects the nanoparticles from oxidation when Cu^{2+} is reduced in irradiation[11].

3.2 Size and morphology of the nano-particles

With PCM concentration of 0.6%, 1.0%, 1.4%, 1.8% and 2.2% (wt.%), $CuSO_4$ aqueous solutions were irradiated to 100 kGy by γ-rays. The size of Cu nanoparticles decreases with increasing PCM concentrations, which were 122.4 nm at 0.6% and 21.3 nm at 2.2% (Fig.1). So changing the particle sizes can be controlled by PCM concentrations.

In Fig.2, TEM images of the products showed that the copper nanoparticles are spherical in uniform size. At lower PCM concentrations, the particle size is larger, but the particle dispersion is better, than those at higher PCM concentrations. The particle size is 15–35nm at PCM concentration of 2.2%.

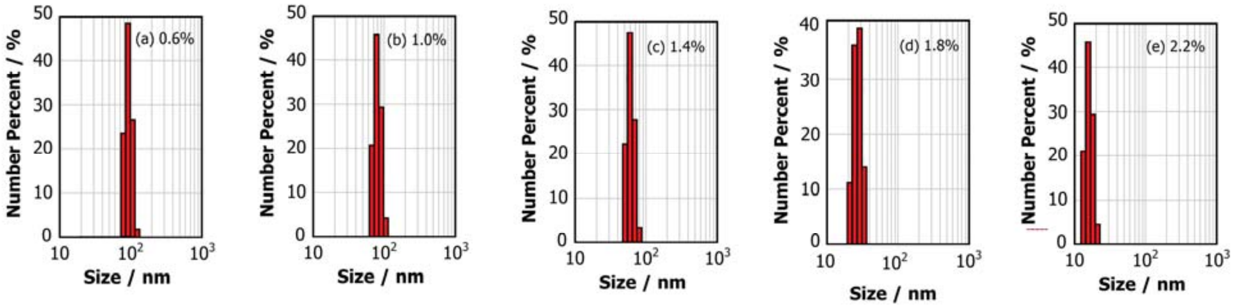

Fig.1 Size of the copper nano-particles prepared with PCM of different concentrations. The data are the mean particle size ±SD.

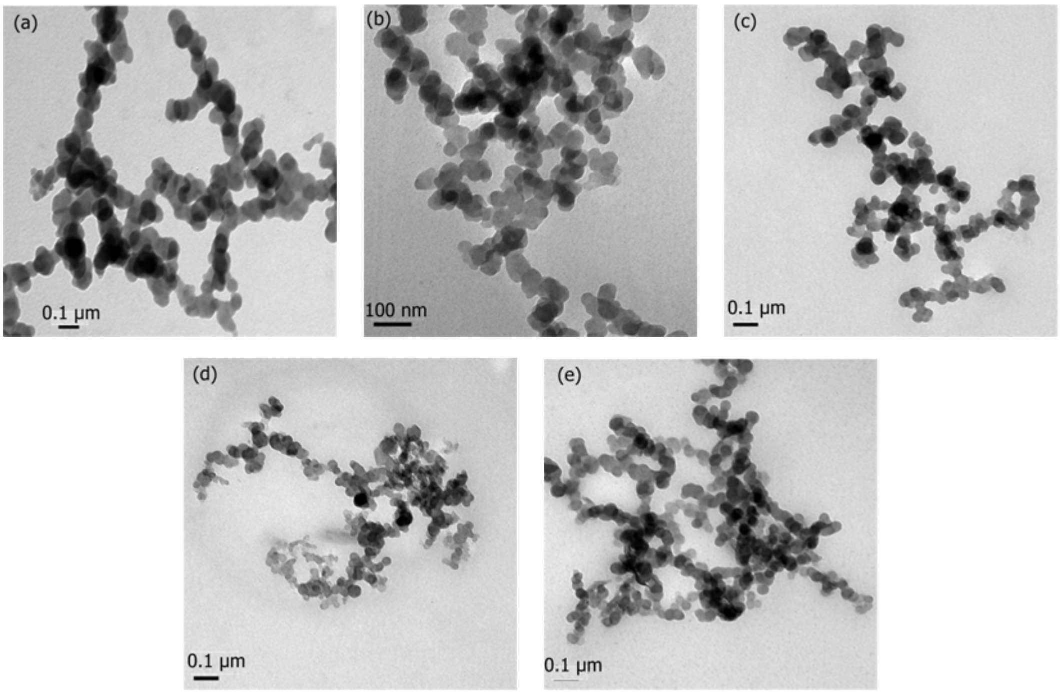

Fig.2 Morphology the copper nano-particles prepared with PCM in different concentrations.

3.3 pH effect on composition of the nanoparticles

With an electrode potential of $Cu^{2+}/Cu = 0.337$ V, nano copper is chemically active. The reduction of Cu^{2+} in γ-ray irradiation produces copper, but there may be some cuprous oxide. In view of this, the aqueous solutions in pH=3.6–10.5 were used for preparing the Cu nanoparticles, which were examined by XRD (Fig.3). The XRD angle of 2θ=43.53°at pH=3.6, 2θ=50.24° at pH=5.1 and 2θ=74.91° at pH=6.5 (Figs.3a to 3c) are consistent with the peaks in the copper standard reference card 01-085-1326, while the XRD angle of 2θ=36.35° at pH=7.5 (Fig.3d) and 2θ=61.36° at pH=9.0 (Fig.3e) angles of the copper are of cuprous oxide, according to the standard reference card 00-005-0667. And the signal of cuprous oxide peak becomes higher, i.e. the Cu_2O content increases, with the pH value. The nano-copper formed in irradiation can be oxidized in air to form cuprous oxide *via* the following reaction,

$$4Cu + O_2 \rightarrow 2Cu_2O \qquad (4)$$

Therefore, pure copper nanoparticles can be prepared at pH= 4–6.5.

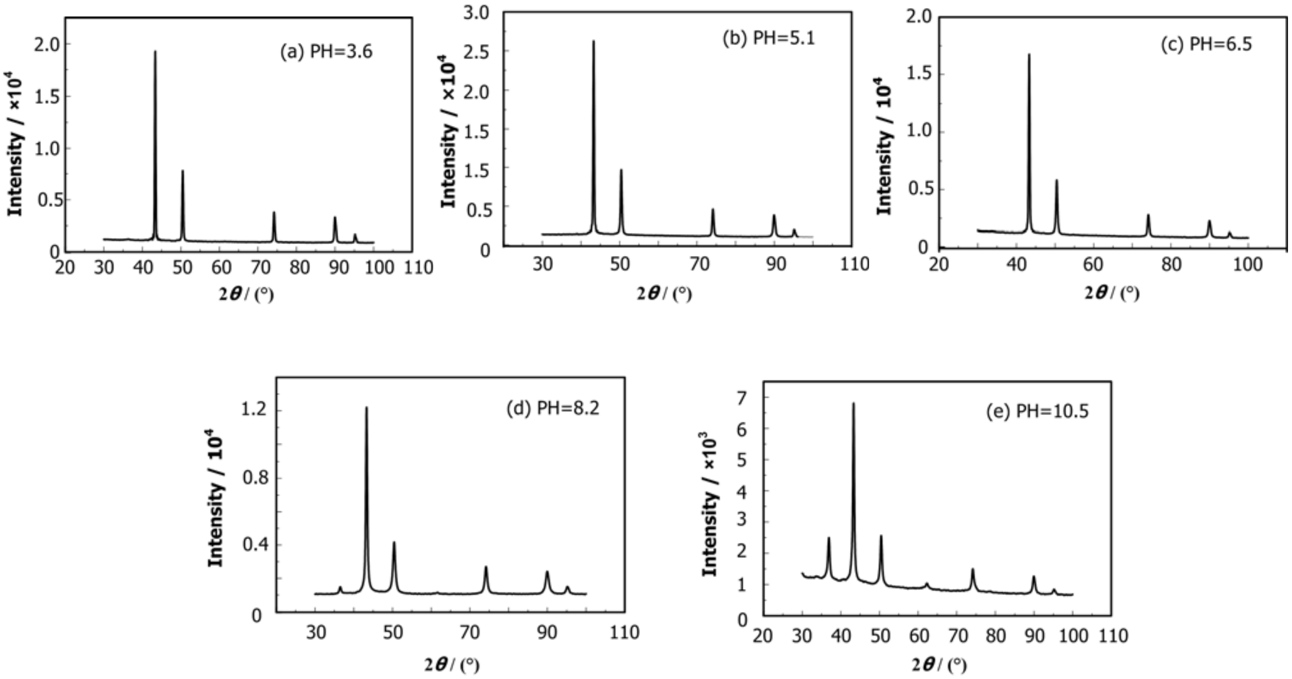

Fig.3 XRD patterns of copper nano-particles prepared at different pH values of the reaction solution.

3.4 Melting point of the nanoparticles

Melting points of the Cu nano-particles were measured by DSC (as shown in Fig.4). They increased with the particle size, with the melting point being 139.90°C, far below the melting point of bulk copper (1083.4°C), at 21.3 nm of particle size, while it is 439.71°C at 122.4 nm.

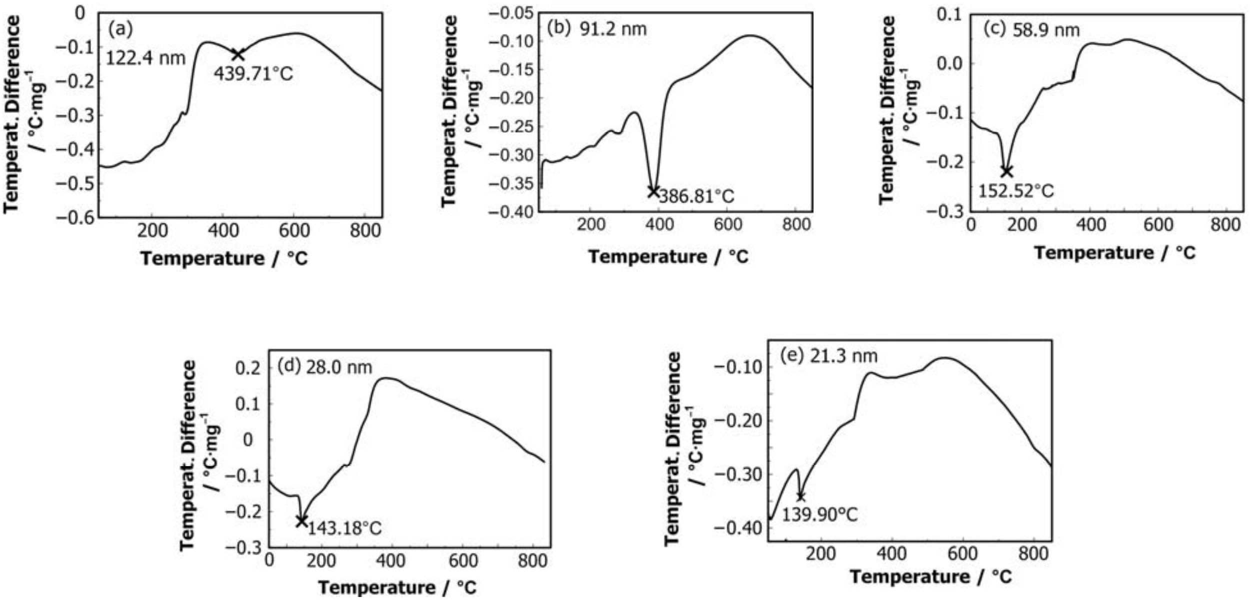

Fig. 4 Melting points of copper nano-particles in sizes of 122.4, 91.2, 58.9, 28.0 and 21.3 nm.

3.5 Stability of the nanoparticles

Copper nano-particles can be oxidized easily in air, so some inactive agents must be added to the aqueous solution for irradiation to protect it from oxidation in aerobic storage condition. We tested with N,N-bis-hydroxyethyl twelve alkyl amide and amine association complexes (referred as N,N-dual-hydroxyethyl dodecyl amide), dodecyl mercaptan, hard fatty acid, oleic acid, oleic acid amide, and castor oil, as inactive agent. The samples protected with different inactive agents were stored in air at room temperature for up to 140 d and checked the phase change with XRD at each time point. Fig.5 shows XRD patterns of the copper powder prepared with dodecanethiol and N,N-bis-hydroxyethyl dodecyl amide, and stored in air for 140 d. There are just characteristic XRD peaks of copper, with no Cu_2O. Both the inactive agents have good antioxidative effect on the copper nanoparticles. Because dodecanethiol is oil-soluble, toxic and expensive, N,N-bis-hydroxyethyl dodecyl amide was chosen as inactive agent.

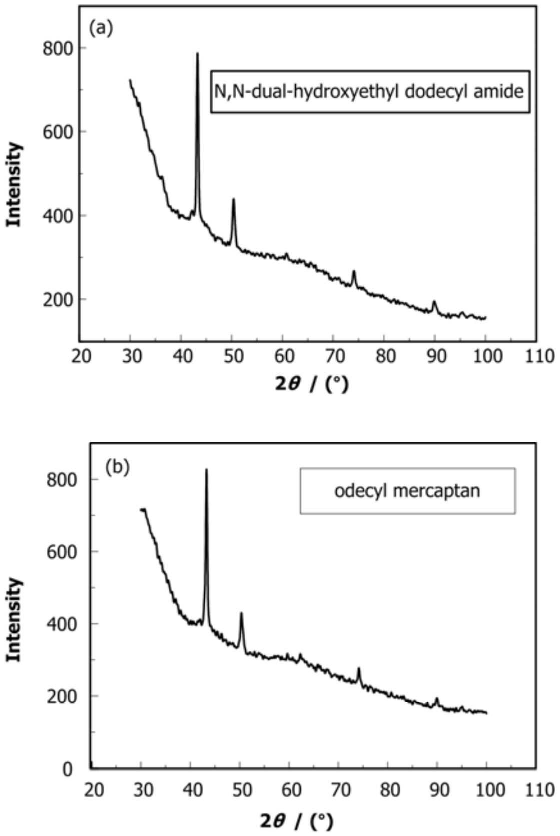

Fig.5 XRD patterns of samples stored for 140 d in air at room temperature.

4 Conclusion

Experimental conditions to prepare Cu nano-particles *via* 100 kGy gamma-ray irradiation have been studies, including the effects of surfactants, passivators and pH values. The following points can be concluded.

Copper nanoparticles can be prepared by γ-ray irradiation of $CuSO_4$ aqueous solution, without any additive of catalysts. Characterizations by XRD, TEM and DSC show that the spherical purple powder of copper is of particle size of less than 100 nm, with melting point of 139.90°C.

Adding PCM surfactant improves dispersion of the nanoparticles. The particle size decreases with increasing PCM concentration, hence the control of particle size by adjusting the PCM concentration.

pH value of the reaction solution should be controlled at 4−6.5, so as to obtain pure Cu nano-particles. Cu_2O would occur at $pH \geq 7.5$.

Using N-dual-hydroxyethyl dodecyl amide association complex as the inactive agent, the copper nano-particles can be stored in air at room temperature for 140 days.

Further efforts shall be made to solve problems in preparing the Cu nano-particles by γ-ray irradiation, such as different composition would reunite with impurities, and some part of the precipitate would be dissolved when washing them with water.

References

1 Li J X, Wu J Q, Yan C. China Ceram, 2002, **38:** 36−39 (In Chinese).

2 Liu H, Ge X, Ni Y, *et al.* Radiat Phys Chem, 2001, **61:** 89−91.

3 Cai S Z, Xia X P, Xie C S. Corros Sci, 2005, **47:** 1039−1047 (In Chinese).

4 Xu X L, Guo J D, Wang Y Z. Mater Sci Eng, 2000, **B77:** 207−209.

5 Chen Z Y, Chen B, Qian Y T. Acta Metallarg Sin, 1992, **5:** 407−410.

6 Li T S, Zhao H Y, Cui G Sh. Chin Mater Sci Equip, 2007, **2:** 42−44 (In Chinese).

7 Yin Y D,, Zhang Z C,, Xu X L, *et a1.*. Chem Online, 1998, **12:** 21−25.

8 Zhang W Z, Wang W G. New Chem Mater, 2003, **31:** 25−28.

9 Lin A, Qin Y M, Rao J, *et al.* Preventive medicine, 2003, **2:** 56−59.

10 Hang J S, R S, Jai J W. J Guangdong Univ Technol, 2005, 22: 7−9 (In Chinese).

11 Qun J R, Hu M G, Chen J Z, *et al.* J China Univ Geosci, 2005, **30:** 195−198 (In Chinese).