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THE SYNTHESIS AND CHARACTERIZATIONS OF NARROW-DISPERSED COPPER NANOPARTICLES

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ABSTRACT

A controlled synthesis method for preparing narrow-dispersed copper nanoparticles, using water and ethylene glycol as the reaction mediums respectively, has been reported. In order to obtain pure-phase copper nanoparticles using water, the reaction time of 8h is essential. Owing to the reduction property of ethylene glycol, the reaction rate using ethylene glycol is higher. In addition, the amount of reduction agent can reduce largely. Polyvinyl pyrrolidone plays great role on the size of copper particles, and the increasing of polyvinyl pyrrolidone concentration attributes to the smaller dimension particles. The mean diameter is about 4 nm when the concentration of polyvinyl pyrrolidone is 0.5 mmol/L. Polyvinyl pyrrolidone acts as the polymeric capping agents in the reaction, preventing the agglomeration of the copper nanoparticles. When water is the reaction medium, Cu^{2+} complex is reduced to Cu^+ complex firstly, and the further reduction of Cu^+ forms the pure copper nanoparticle.

INTRODUCTION

In recent years, much attention has been paid to metal nanoparticles which exhibit novel optical, electronic, magnetic, and chemical properties owing to their extremely small dimensions and their special surface [1-3]. Among these metal materials, copper-based materials are becoming increasing attractive for both fundamental research and practical purposes. For example, copper nanoparticles can improve the brittleness of the phenol-formaldehyde (PF) resins obviously, and improve the thermal stability of the PF resins at lower temperatures [4]. Copper nanoparticles have antibacterial capabilities, and Cu/Sepiolite particles can decrease the starting microorganism concentrations of *Staphylococcus aureus* or *Escherichia Coli* by 99.9% [5]. Small copper particles embedded in oxide glasses strongly modify their optical properties, making these composite materials useful for resonant-type non-linear optical materials for photonic devices [6]. Copper nanoparticles are good additive of nanofluid, which is produced by dispersing nanoparticles into conventional heat transfer fluids, and nanofluids are proposed as the next generation heat transfer fluids due to the fact that their thermal conductivities are

significantly higher than those of the base liquids [7, 8]. As a result, many efforts have been directed toward the synthesis of copper nanoparticles. The synthesis has been achieved via various reduction routes, including radiation methods, microemulsion techniques, sonochemical reduction, laser ablation, vacuum vapor deposition, thermal decomposition, chemical reduction etc [9-11]. Among these methods, chemical reduction is one of the most convenient methods for synthesis of copper nanoparticles [12], due to simpleness of technics and low cost, and it yields a large variety of dispersions in terms of their particle characteristics (size, morphology, stability) by various the different experimental parameters (concentration, redox potentials, temperature, pH etc).

It is well known that the size and morphology are important factors in determining the physical and chemical properties of particles. Thus controlled synthesis of copper nanoparticles has moved into focus [13-17]. Here, we report a facial chemical reduction method to synthesize narrow-dispersed copper nanoparticles. Two reaction mediums, water and ethylene glycol, was used as solvents, and the influences of solvents on reaction rate, the amount of reduction agent and reaction mechanism were discussed.

EXPERIMENTAL

Copper sulfate, vitamin C (VC), polyvinyl pyrrolidone (PVP-K30, Mw = 40,000) and ethylene glycol (EG) were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. All of the chemicals were analytical grade and used as purchased without further purification. In the experiments, copper nanoparticles were synthesized by two procedures, using deionized water and EG as reaction solvents, respectively. In a typical procedure, a certain amount of PVP and VC was dissolved in the 200 mL 0.1 M CuSO_4 aqueous (or EG) solution under mechanical stirring, and the reaction mixture was aged at 80°C for some time. The colloidal suspension was then taken out from the oil bath and cooled to room temperature. After that, the suspension was diluted by ethanol absolute and centrifugated at 8000 rpm for 15 min to separate the particles in the suspension. The particles separated were then resuspended in ethanol absolute and the centrifugation was

repeated thrice so as to remove the surfactant. After that, the precipitates were dried under vacuum overnight and collected for further characterization. The experimental parameters are listed in Table 1, and the corresponding XRD patterns of the products prepared at different experimental parameters are shown in Fig. 1.

2.2 Characterization of copper nanoparticles

XRD measurements were recorded using a (D8-Advance, Germany) X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source ($\lambda = 0.154$ nm). XRD patterns were recorded from 20 to 80 (2θ) with a scanning step of 0.01. The size and morphology of the Cu nanoparticles were examined by using transmission electron microscopy (TEM, JEOL 2100F). The TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping the suspension onto a holey carbon film supported on a copper grid, and drying it in air.

RESULTS AND DISCUSSION

Table 1 Comparison of results from the two reaction systems and different experimental parameters

| Sample No./ time | Solvent | PVP-K30 (mmol/L) | VC/Cu ²⁺ (mol/mol) | Mean size (nm) |
|------------------|---------|------------------|-------------------------------|----------------|
| 1/3h | water | 0.5 | 20 | -- |
| 2/6h | water | 0.5 | 20 | -- |
| 3/8h | water | 0.5 | 20 | 7±3 |
| 4/1h | EG | 0.1 | 8 | 25±5 |
| 5/1h | EG | 0.3 | 8 | 10±3 |
| 6/1h | EG | 0.5 | 8 | 4±1 |

Sample 1 to sample 3 were synthesized using water as solvent, and the reaction time was 3h, 6h and 8h, respectively. The reaction rate using water as solvent was slow, because VC was a weak reduction agent. The light blue reaction system turned to cloudy yellow in 3 hours, and then it became brick red, and after 2 hours it became red colloidal with some precipitation in the bottom. The XRD patterns of samples prepared by different procedures are shown in Fig. 1. When the reaction time was 3h and 6h, the product was impure, and it was the mixture of face-centered cubic (fcc) phase of copper (JCPDS 04-836) copper and cubic phase of Cu₂O (JCPDS 05-0667), and copper was the main product. The XRD analysis results coincided with the experimental phenomena. When the reaction time was 8h, the product was pure, and three main characteristic diffraction peaks for copper at $2\theta = 43.2, 50.4$ and 74.0 degree, corresponding to (111), (200) and (220) crystal planes respectively were observed. This confirmed the formation of fcc copper nanoparticles, and no impurity diffraction peaks were detected.

Comparing to the reaction rate using water as solvent, the rate using EG was higher. In 15 minutes, the initial precursor solution with light blue color changed to light brown, red, black. Then, there was no further color change, and the reaction could complete in 1h, and the product was phase-pure. The higher rate using EG attributed to the reduction property of EG.

EG was a weak reduction agent, and it could reduce Cu²⁺ to Cu⁺, which was confirmed by some experimental facts [18 19]. Due to the united deoxidization of VC and EG, the reaction using EG was fast, and Cu₂O was not detected in the procedure. In addition, the amount of reduction agent VC could reduce largely. When water was solvent, the molar ratio of VC/Cu²⁺ was up to 20. For EG reaction system, the molar ratio of VC/Cu²⁺ was 8, and the yield was about 95%.

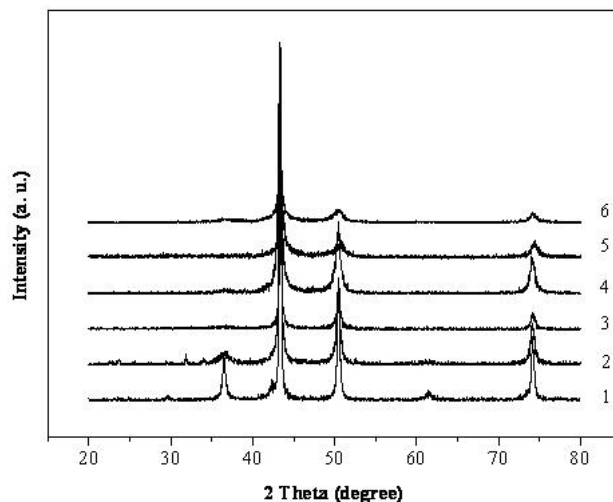
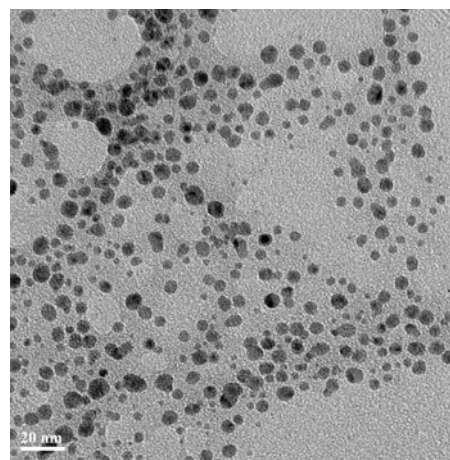
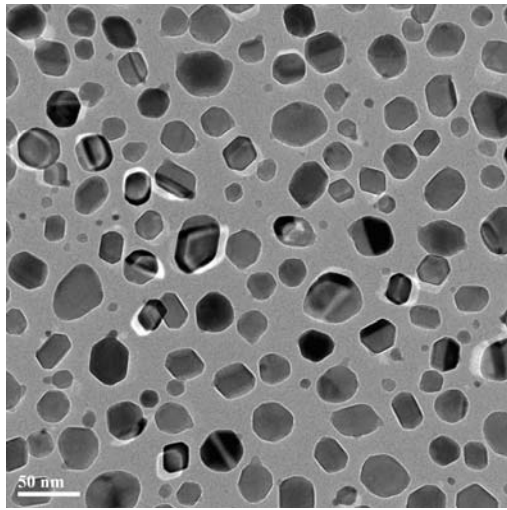


Fig. 1. XRD pattern of the products prepared at different experimental parameters.

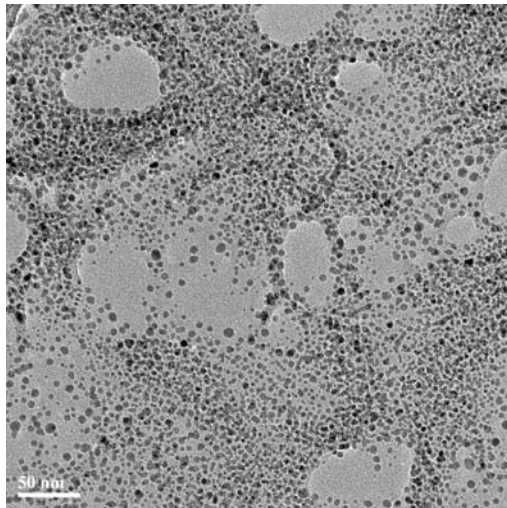
It is well known that PVP is an important dispersant to prepare nanomaterials, and the size and shape of nanomaterials depends strongly on the solution concentration of PVP [20, 21]. When water was the reaction solvent and the concentration of PVP was 0.5 mmol/L, the copper nanoparticles were approximately spherical with the diameter about 7 nm, which is shown in Fig.2-(a). Owing to the slowness of reaction and waste of much reduction agent using water as solvent, much attention was focused on the influence of PVP on the size of copper nanoparticles using EG as reaction medium (Fig.2-(b), (c) and (d)). The copper nanoparticles were narrow-dispersed in EG reaction system, and the mean diameters were about 25, 10 and 4 nm, respectively, when the concentration of PVP was 0.1, 0.3 and 0.5 mmol/L, indicating that the increasing of PVP concentration attributes to the smaller dimension particles.



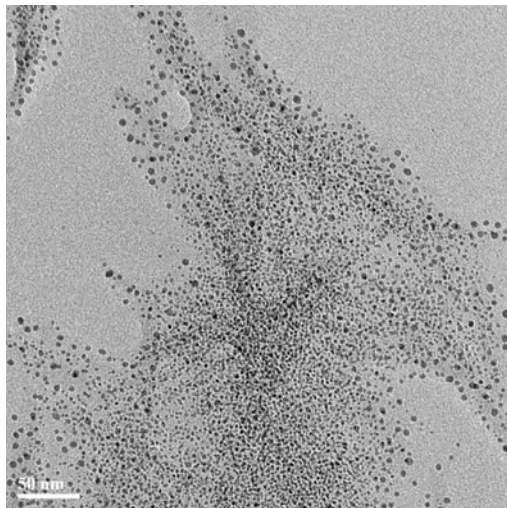
(a)



(b)



(c)

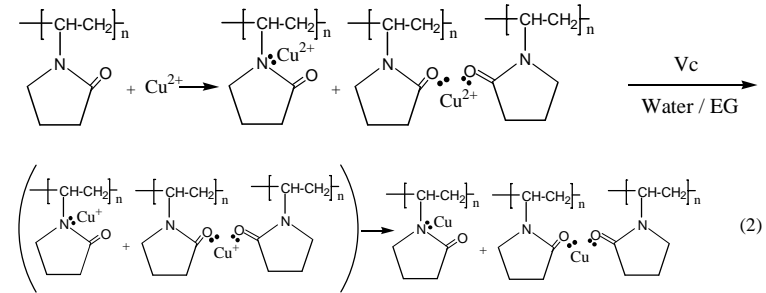


(d)

Fig. 2. Typical TEM images of Cu nanoparticles. (a) sample 3; (b) sample 4; (c) sample 5; (d) sample 6.

The mechanism of the effect of PVP on size and shape of nanomaterials has been discussed in some literatures [22-24]. PVP has the structure of a polyvinyl skeleton with nitrogen and oxygen polar groups, and the polar group donates lone-pair

electrons forming a coordinative interaction with copper ions, thus creating the Cu^{2+} -PVP complex compound (Eq. 1) in the solution. When water was the reaction medium, the reaction time was 3-6 h, according to the XRD analysis, the product was impure, indicating that Cu^{2+} -PVP complex was reduced to Cu^+ -PVP firstly, and then Cu^+ reacted with OH^- to form Cu_2O , due to the existence of enough OH^- , so the color of reaction system was yellow when the reaction time was 3 h. The further reduction of Cu^+ formed the pure copper nanoparticle. The coordination action between PVP and Cu^+ prevented the agglomeration of the copper nanoparticles (Eq. 2). Due to the higher rate using EG as reaction medium, no intergradation product Cu_2O was detected. According to the above analysis, PVP acted as the polymeric capping agents in the reaction.



CONCLUSIONS

In this paper, two procedures for preparing narrow-dispersed copper nanoparticles, using water and EG as the reaction mediums respectively, has been reported. In order to obtain pure-phase copper nanoparticles using water as solvent, the reaction time of 8h is essential; otherwise the products will be the mixture of face-centered cubic phase of copper and cubic phase of Cu_2O . Comparing to the reaction rate using water, the rate using EG was higher, due to the reduction property of EG. In addition, the amount of reduction agent VC could reduce largely. The size of copper particles depended strongly on the solution concentration of PVP, and the increasing of PVP concentration attributed to the smaller dimension particles, and the mean diameters of particles was about 4 nm when the concentration of PVP is 0.5 mmol/L. The mechanism of the effect of PVP has been discussed, and it acts as the polymeric capping agents in the reaction, preventing the agglomeration of the copper nanoparticles. When water is the reaction medium, Cu^{2+} -PVP complex is reduced to Cu^+ -PVP firstly, and the further reduction of Cu^+ formed the pure copper nanoparticle.

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