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Influence of ascorbic acid on the stabilization of the copper suspension colloids

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In this paper, copper suspension colloids were prepared via single chemical reduction method without protective gas. In this procedure, the influence of ascorbic acid (VC) as antioxidant and dispersant dissolved in the aqueous copper colloids on the colloidal stabilization was studied by X-ray diffractometry (XRD), UV-vis spectrophotometer (UV-vis) and transmission electron microscopy (TEM), respectively. The results revealed that VC plays important role of protecting the copper colloids to prevent oxidation and agglomeration, and the VC-protected copper suspension colloids have good stability for application.

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Keywords: Copper colloids, Ascorbic acid, Oxidation resistance, Dispersion

1. Introduction

Recently, copper colloids are paid more and more attentions, based on their specific electronic structure, charge distribution and large specific surface. So far, copper colloids have exhibited characteristic spectra due to surface plasmon resonance nanofluids, and have been dispersed into conventional heat fluids as a good thermal conductive additive. Furthermore, the aqueous copper suspension colloids can activate non-conductive substrates for subsequent electroless plating instead of palladium colloids for its lower price [1, 2].

The copper colloids are prepared by various processes such as chemical reduction, sono-chemical reduction, Seed-mediated growth, thermal reduction, γ-radiation and ultra-visible light irradiation, in the presence of vacuum or protective gas [3]. Compared with noble metals, such as Ag and Au, copper suspension colloids usually cannot be obtained easily by using the simple reduction of copper salts in aqueous solution. The main question arises from the stability of copper colloids including the extremely sensitive to oxygen and colloidal agglomeration. Therefore, there are several approaches related to the dispersions and oxidation resistance that need to be solved before application. One approach is preparation of copper colloids in aqueous solution containing polymers or surfactant as stabilizer such as polyvinyl-pyrrolidone (PVP) K-30, polyvinyl alcohol, hexadecyl trimethyl ammonium bromide and so on [4]. Another approach is addition of ascorbic acid (VC) as a antioxidant to protect the copper colloids, related to few literatures [5].

Despite that oxidation resistance and dispersions are of immense importance in several applications, but few studies have been carried out in this area and there are no clear guidelines for how to improve stability. In the present work, the influence of VC on the oxidation and dispersions of the aqueous copper colloids were investigated. Copper colloids were prepared with single chemical reduction method without protective gas, and VC as a stabilizer added to the aqueous copper colloids was studied by XRD, UV-vis and TEM.

2. Experimental

2.1 Materials

The reagents were copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, AR grade), sodium borohydride ($NaBH_4$, 96%, CP grade), ascorbic acid (VC, 99%, AR grade) and polyvinyl-pyrrolidone (PVP) K-30(PVP-K30, Mw = 40,000). In the process of experiments, distilled water was used, and all the solvents were used without further purification.

2.2 Synthesis of copper colloids

The aqueous copper colloids were prepared using the single chemical reduction method as follow. Typically, 5.0g PVP-K30 was dissolved in the aqueous solution of $CuSO_4 \cdot 5H_2O$ (0.25g in 100ml distilled water). $NaBH_4$ (0.25g), used as a reducing agent, was put into the above mixture with stirring at room temperature. Initially the blue color of the reaction mixture changed to green, and eventually turned brown. After incubating for 15 min, an appropriate amount of VC was added to the above-prepared solution, and the reaction mixture was kept at 60℃ for 30min. For further characterization, the colloid was diluted by ethanol and centrifuged at 4000 rpm for 15 min to separate the copper colloidal particles from the aqueous suspensions.

2.3 Characterization

Digital images of samples were obtained by an AIGO T1028 digital camera. Electron microscopy images were acquired on a HITACHI H-800 transmission electron microscopy (TEM) with an accelerating voltage of 100kv. X-ray diffraction (XRD) patterns were taken on an SHIMADZU XRD-6000 X-ray diffractometer, with CuKα (λ=1.54056Å) radiation being used at 40kv and 30 mA. UV-visible spectroscopy (UV-vis) spectra were measured in a SHIMADZU UV-2550 UV-vis spectrometer.

3. Results and discussion

3.1 Morphology and crystal structure of the copper colloids

Fig. 1 shows the TEM images of the as-prepared copper colloids after separating from the suspensions. It can be seen that the copper colloids produce agglomeration after separation and dryness (in Fig.1A), and the copper colloids are approximately spherical with the size about 20nm visualized by low-contrast fuscous spots surrounding the agglomerates (in Fig.1B).

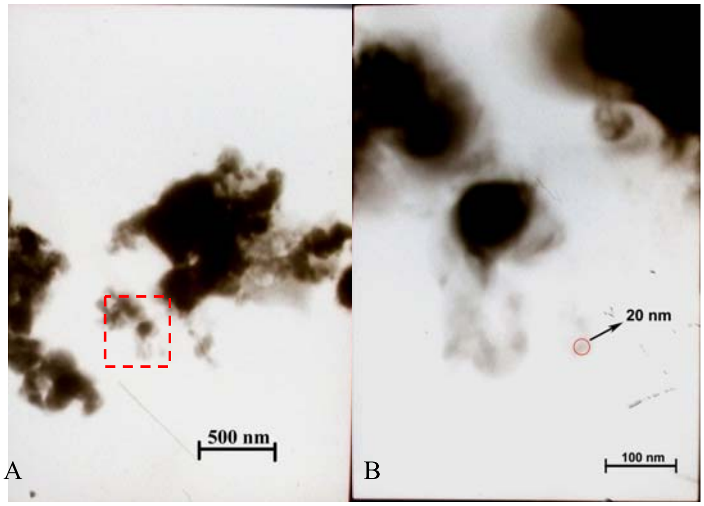

Fig. 1. TEM images of the VC-protected copper colloids (A) and the magnified part (B).

The crystal structure of copper colloids was indicated by XRD pattern as shown in Fig. 2B. The VC-protected copper colloids are determined to only copper without any other phase such as CuO, Cu_2O, or $Cu(OH)_2$, in contrast of the bulk copper. All possible peaks of copper are observed, which indicates the polycrystalline nature of the product. Bragg's reflections for copper colloids are observed in XRD pattern at 2θ value of 43.6°, 50.7° and 74.5° representing [1 1 1], [2 0 0] and [2 2 0] planes of fcc structure of copper with the space group of Fm3m (JCPDS No. 4–0836). The crystallite size measurements were also carried out using the Scherrer equation, $D=k\lambda/\beta\cos\theta$, where D is the crystallite size, k is a constant (=0.94 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, ß is the line width at half maximum intensity of the peak and θ is the angle of diffraction. The mean size of the copper crystallites was estimated from Scherrer equation to be 15 nm.

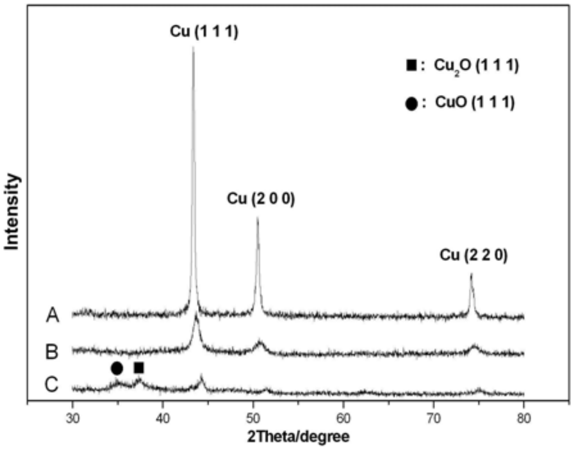

Fig. 2. XRD patterns of the bulk copper (A), VC-protected copper colloids (B), and as-prepared copper colloids without VC(C).

3.2 Influence of VC on the copper colloidal oxidation and dispersion

Fig. 3 displays the color change of different VC antioxidant solution. All the samples were taken after depositing 30min. It can be seen that the effect of VC is obvious: the samples return the blue Cu^{2+} solution or become the black agglomerates without adding VC(Fig.1A and B), and the colors turn from light brown to brown with increasing the amount of VC over the range of 4.4-35.4 g/L (Fig.1C-G). The brown samples are copper suspension colloids, related to statements of 3.1. By diffraction angles measurement (Fig. 2C) and comparison with standard reference card, it can be found that the black agglomerates are a mixture of Cu, Cu_2O and CuO. The results demonstrated that the actions of heating are to accelerate the agglomeration and the reactive rate of oxidation, and the VC plays a role of antioxidant to protect the copper colloids without protective gas. The antioxidant properties of VC come from its ability to scavenge free radicals and reactive oxygen molecules, accompanying the donation of electrons to give the semi-dehydroascorbate radical and dehydroascorbic acid [6].

Fig. 3.The color change of different VC antioxidant solution from bottle A-G: 0(without heating), 0, 4.4 g/L, 8.8g/L, 17.6g/L, 26.4g/L, 35.2g/L.

On the other hand, it was also shown that the VC-protected copper suspension colloids have good dispersions in Fig. 3C-G. The noble metal colloids such as gold and silver, can stably disperse in the aqueous solution in the absence of special protected agent and gas due to the inactivity of elements. The chemical properties of the copper colloids with VC antioxidant protection should be similar to the silver or gold in the same subgroup, so the as-prepared copper colloids become stable in the aqueous solution, too. In other words, the oxidation resistance of VC affects the dispersion of the colloidal copper.

3.3 Influence of storage time on the copper colloidal stabilization

In order to further study the influence of VC on the stabilization, the VC-protected copper suspension colloids were placed at room temperature for some days. Fig. 4 displays the influence of storage time on the VC-protected aqueous copper colloids by using 35.2g/L VC. It can be seen than the dispersions of samples are invariable in 10d, but the brown products turn light brown in 3d, then red in 7d and then light red in 10d. Moreover, according to the UV-vis spectra analysis, the resonance absorption peaks weaken and exhibit blue shift from 575nm to 565nm along with the storage time. It is suggested that the diameters of the as-prepared copper colloids gets slowly smaller for storage. The probable reason is the change of pH [7, 8]. During the storage, the pH changed from initial 6.2 to 5.0 to induce the change of colloidal size.

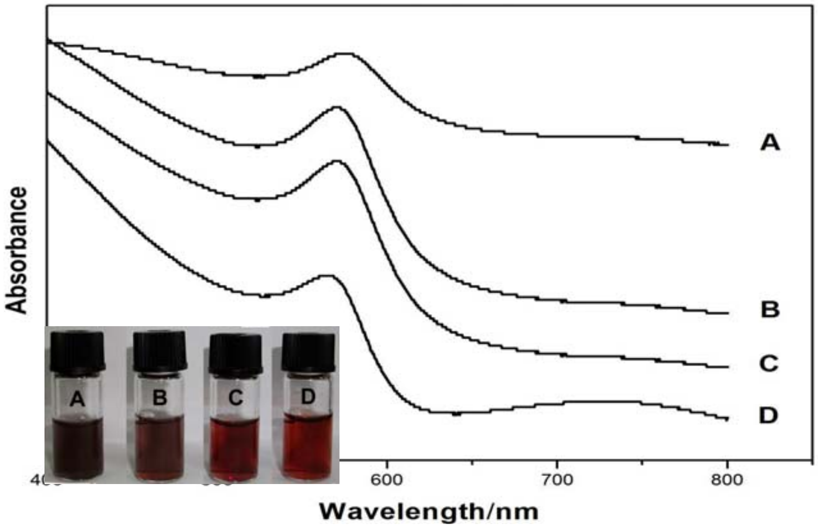

Fig. 3. The color change of the VC-protected copper suspension colloids and corresponding UV-vis spectra with different storage time: (A) new-made, (B) stored 3 d, (C) stored 7 d and (D) stored 10 d.

4. Conclusions

In summary, the stable copper suspension colloids could be prepared according to single chemical reduction method without protective gas that depends on the protection of ascorbic acid. Ascorbic acid has significant influences on the antioxidation and dispersions of the aqueous copper colloids, and enough ascorbic acid is essential to protect copper suspension colloids, which will keep enough time stable for application.

Acknowledgements

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