

Synthesis of Highly Stable Dispersions of Copper nanoparticles Using Sodium Hypophosphite

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ABSTRACT: Highly stable dispersions of copper nanoparticles with an average diameter of 80 nm were synthesized using a straightforward and cost-effective method in the presence of polyvinylpyrrolidone (PVP) as a stabilizer and without any inert gas protection. Sodium hypophosphite was used as the reducing agent in low pH value aqueous medium. The copper nanoparticles were characterized by ultraviolet-visible spectroscopy and scanning electron microscopy. The mechanism of the PVP on the stabilization of copper nanoparticles is also discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Metal nanoparticles have attracted much attention in nanoscale science and engineering technology in the past two decades because of their unusual properties and potential applications.^{1–8} Their main application areas include catalysts, absorbents, chemical and biological sensors, optoelectronics, information storage, and photonic and electronic devices.^{9–14}

A number of methods had been developed to synthesize metal nanoparticles, such as solvent extraction reduction, photolytic reduction, radiolytic reduction, wet chemical reduction, sonochemical method, microemulsion techniques, polyol processes, alcohol reduction, and laser ablation.^{15–28} Among the above methods, the wet chemical reduction method has the advantage over the others in easy control of the reaction process and production rate. The wet chemical reduction method is mostly achieved by reduction of a metal ion salt solution. But most of wet chemical reduction methods reported to date rely heavily on organic solvents,^{29–33} which will cause the secondary pollution due to the evaporation and have an adverse effect on the further applications sometimes. On the contrary, with water as the solvent, the secondary pollution and some adverse effects of the organic solvent can be avoided.

Copper nanoparticles (Cu-NPs) play an important role in many applications such as thermal transfer nanofluids, lubricants, catalysts, electronic materials, and optical devices.^{34–40} The hydrazine,⁴¹ sodium borohydride,¹³ and L-ascorbic acid^{14,42} are

frequently used as reductants. However, these reductants are expensive. Therefore, there is a need for more economical reductants for the preparation of copper nanoparticles. Sodium hypophosphite is extensively used as reductant in the electroless plating for low price. Lee et al.³² had prepared Cu-NPs in ethylene glycol and Park et al.¹⁹ in diethyleneglycol using sodium hypophosphite as the reductant. They obtained Cu-NPs with a diameter about 50 nm but the Cu-NPs solution did not have high stability. Throughout the literature review, we did not find any report about preparation Cu-NPs of high stability and good dispersion in aqueous solution using sodium hypophosphite as the reductant.

Using soluble polymers or surfactants as capping agents to prepare Cu-NPs in aqueous solutions was attractive. However, until now, only few works have been done because copper is easily oxidized.⁴¹ To avoid oxidation, the synthesis of Cu-NPs were usually performed in nonaqueous media, at low-precursor concentration and under an inert atmosphere. All these syntheses of Cu-NPs involve using of strong reducing reagents with protecting gases. One synthesis that did not use protecting gases was the reduction of CuCl₂ with N₂H₄ in aqueous cetyltrimethylammonium bromide (CTAB) solution.⁴¹ In this reaction, the N₂ released during the reduction process auto-created an inert atmosphere. Yet oxides would be produced if the process was performed in an open bottle. In another synthesis of Cu-NPs, the L-ascorbic acid was used as both a reducing agent and capping agent precursor in aqueous medium.⁴²

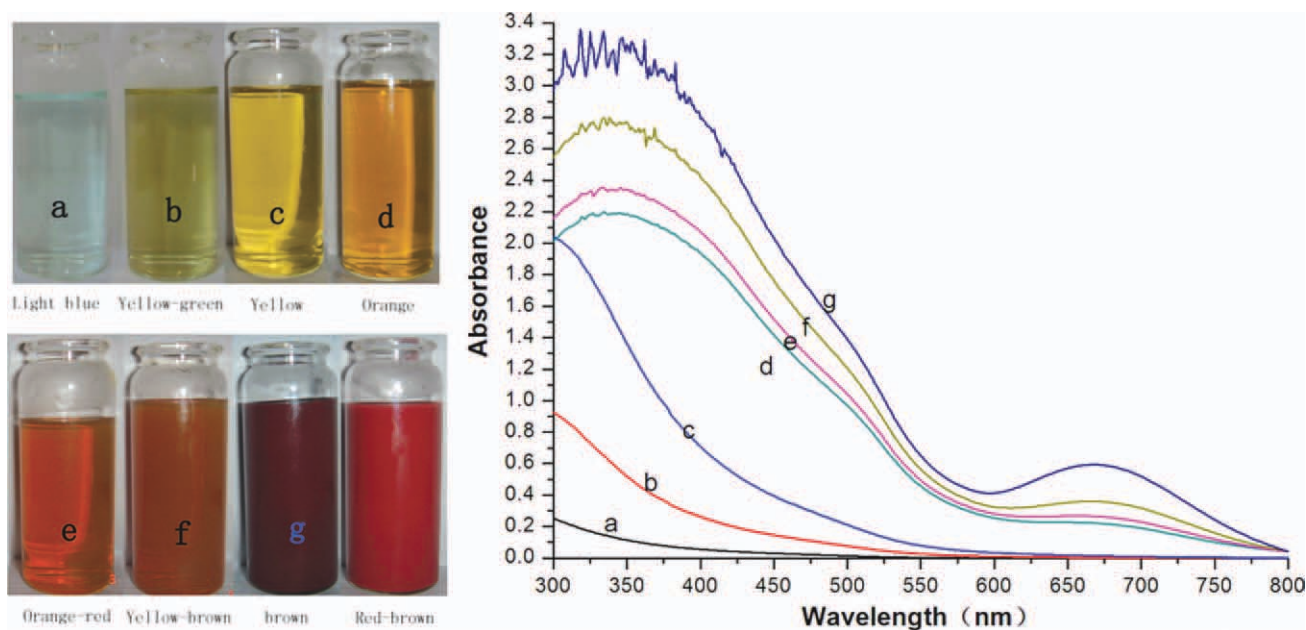


Figure 1. The time evolution of the dispersion photographs and the UV-Vis absorption spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In this research, the polyvinylpyrrolidone (PVP) coated Cu-NPs was synthesized by a wet chemical reduction method in acidic aqueous solution with sodium hypophosphite as the reducing agent. The PVP coating and the acidic conditions can protect the Cu-NPs from oxidation and make the Cu-NPs high stability and good dispersion.

EXPERIMENTAL

Materials

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Hangzhou Xiaoshan Chemical Reagent Factory) acted as the precursor for the formation of Cu-NPs. $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (Sinopharm Group Chemical Reagent) acted as reducing agent and PVP (Huipu Chemical Instruments k90) acted as capping agent. Deionized water was used in all experiments.

Preparation of Cu-NPs

In a typical preparation process, the aqueous solution was prepared by dissolving $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (2 g), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.1 g), and PVP (0.55 g, 1.1 g, 2.2 g, 4.4 g) in 100 mL deionized water at the flask and added H_2SO_4 into the flask while stirring to adjust the pH value to 1. The mixture was kept at 65°C in a water bath with magnetic stirring until a red-brown solution was obtained. One part of the resulting dispersion was treated three times as the follow step for the X-ray powder diffraction (XRD) characterization: centrifuged at 8000 rpm for 20 min with acetone added in and then washed with alcohol and deionized water. Other part was placed under ambient conditions for 2 months.

Characterization

The UV-Vis absorption spectra of the produced dispersions were recorded on a UV-3010 spectrophotometer. The morphology and size of the as-synthesized Cu-NPs were characterized by scanning electron microscopy (SEM, JEOL), transmission electron microscopy (TEM, JEOL, Japan, JSM-2100), and high

resolution transmission electron microscopy (HRTEM). The crystallographic structure of the products was determined using XRD (Switzerland Thermo, ARL XTRA).

RESULTS AND DISCUSSION

UV-Vis Studies on Cu-NPs

UV-Vis absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak positions and shapes are sensitive to particle size. The light-blue dispersion became colorless when the H_2SO_4 solution was added, and gradually turned to yellow-green, yellow, orange, orange-red, yellow-brown, brown, and finally red-brown (see Figure 1). The regulation of color change was in accordance with the report of Xiong.⁴² The UV-Vis absorbance spectroscopies of the dispersion in different reaction stage are shown in Figure 1. The first absorption peaks of different curves were all at around 350 nm corresponding to the oxidation product of sodium hypophosphite. This can be provided by another experiment that designed by Xiong,⁴² in which H_2O_2 was used as oxidant to react with L-ascorbic acid, and the product showed single peak at around 330 nm. When the H_2O_2 was used as oxidant react with sodium hypophosphite, and the product showed single peak at around 350 nm.

The surface plasmon peak of Cu-NPs has been reported to be appear at around 570 nm.⁴³ However, in our work, the second absorption peaks were increasingly heightening with the reaction time and the resulting brown copper dispersion did not show a plasmon peak at around 570 nm, but displayed a broadened peak at 668 nm. When the dispersion became brown, the UV-Vis absorption spectra of the produced dispersions were recorded every 20 min, and shown in Figure 2. As can be seen from the absorption spectra that the plasmon peak demonstrated an anomalous blue shift from 668 nm to 599 nm along

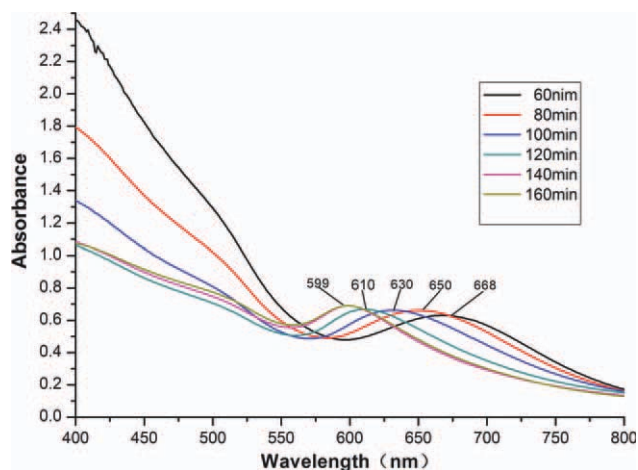


Figure 2. The UV-Vis absorption spectra of the Cu-NPs with the reaction progressing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the increase of reaction time and a very weak peak appeared in the 500 nm. The reaction (including the reduction reaction process and Cu-NPs growth process) was completed after 140 min as the UV-Vis absorption curves of 140 min and 160 min almost overlapped and the dispersion became red-brown.

In the theory of Ostwald ripening, the second absorption peaks had an intensity increase and red-shift with the reaction pro-

gressing due to the growth of Cu-NPs in the ordinary synthesis. So this UV-Vis absorption spectra may be inferred another mechanism of the growth of Cu-NPs. Ellipsoidal metal nanoparticles often show two absorption peaks.⁴⁴ The transverse absorption peak was weak and its position did not change with the aspect ratio of the ellipsoidal metal nanoparticles. Another longitudinal plasma absorption peak position changed with the aspect ratio obviously and it would red-shift with the increasing aspect ratio. Based on the above results, we can infer that the blue shift from 668 nm to 599 nm was attributed to the decreasing aspect ratio of the ellipsoidal Cu-NPs. The possible mechanism may be that the ellipsoidal Cu-NPs growing up when the dispersion became yellow-brown and red-brown, but converted to the spherical in the stage of Ostwald ripening that made the aspect ratio of the ellipsoidal Cu-NPs decreasing.

In addition, no enhanced background absorption around 800 nm can be observed implicating that the colloidal particles were nominally reduced copper in nature without being oxidized to copper oxide on surface.⁴⁵ This was attributed to the low pH value.

Size and Morphology Analyses

The morphology and the size distribution of the collected particles were studied using SEM. Figure 3 showed the typical SEM images of the as-synthesized Cu-NPs. The observed patterns indicated that Cu-NPs were rather monodispersed in nearly sphere shape. Furthermore, the particle size was decreased with the increase of PVP concentration. The sizes of the Cu-NPs

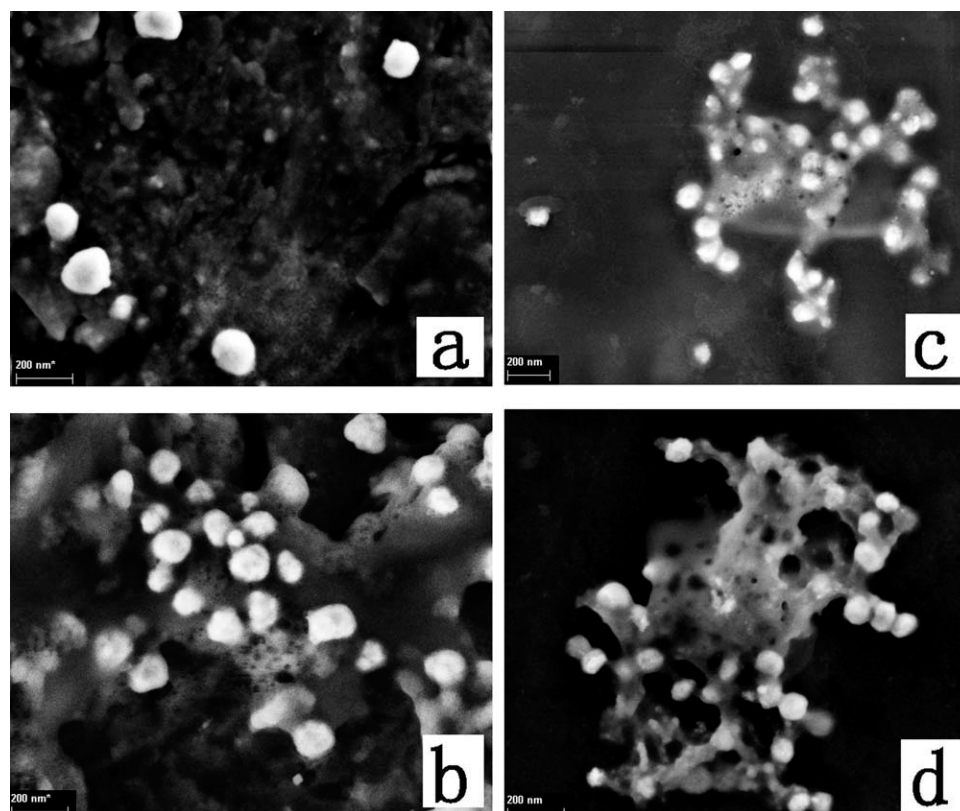


Figure 3. SEM images of the synthesized Cu-NPs with various concentrations of PVP: (a) 0.05 M; (b) 0.1 M; (c) 0.2 M; (d) 0.4 M.

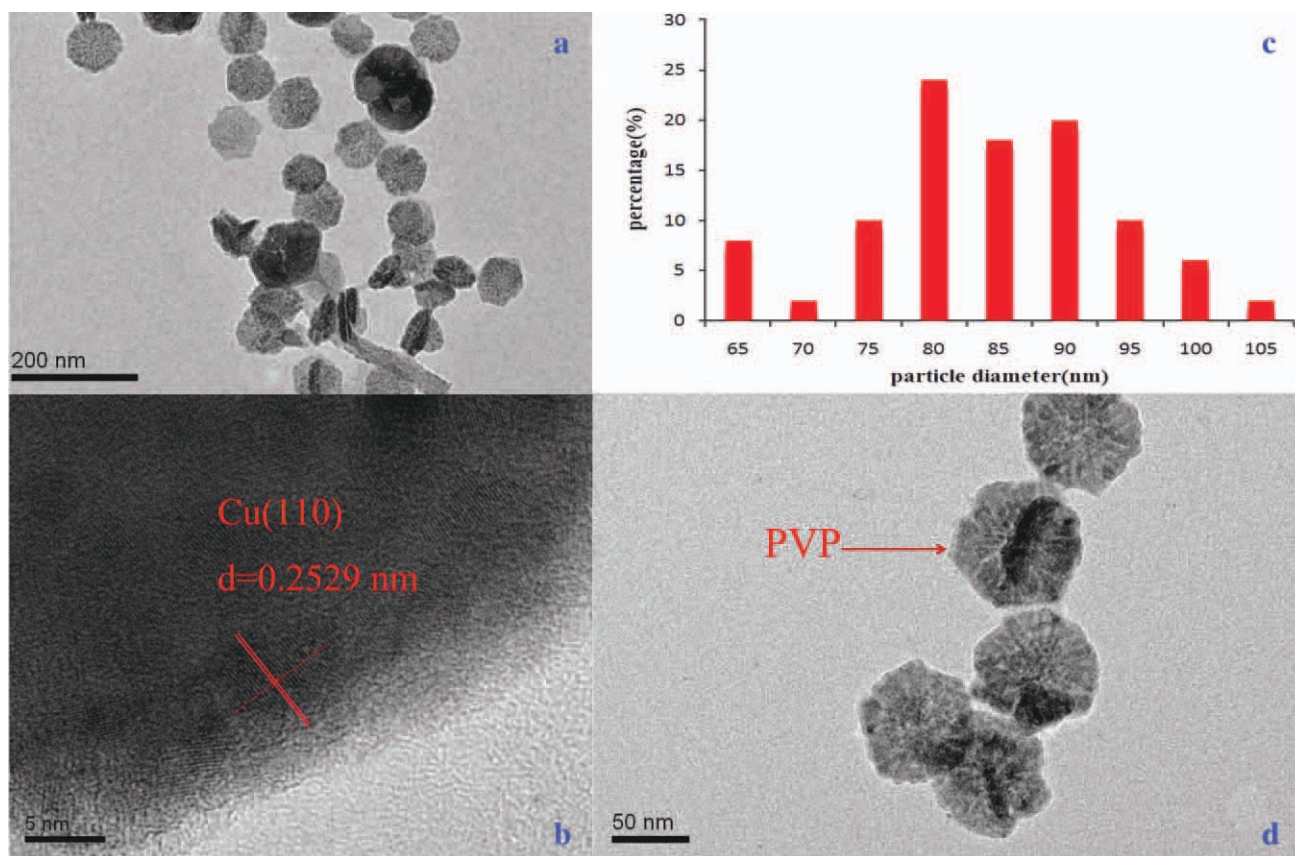


Figure 4. (a, d) TEM images of the morphology of the Cu-NPs and (c) the corresponding particle size distribution of Cu-NPs. (b) The HRTEM image of Cu-NPs. The reduction time of the sample is 160 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with various concentrations of PVP (0.05 M, 0.1 M, 0.2 M, and 0.4 M) were about 150 nm, 140 nm, 90 nm, and 80 nm respectively. The reason was that PVP molecules encapsulated Cu^{2+} and adsorbed on the resulting Cu-NPs surfaces, preventing the particles from growing further. With the increasing concentration of PVP, the number of Cu^{2+} encapsulated in PVP molecules decreased, leading to the formation of smaller Cu-NPs (which will be further discussed in the mechanism section).

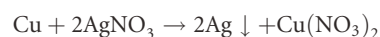
When the concentration of PVP increases to 0.1 M, the PVP cannot be removed completely by centrifugation of the sample at 8000 rpm for 20 min with acetone added and then washed with alcohol and deionized water for three times. As can be seen from the Figure 3. The possible reason was that the PVP-k90 has high molecular weight and chelates with the Cu-NPs, and this made it difficult to be removed completely.

The TEM images of Cu-NPs were shown in Figure 4. Figure 4(a) portrayed the morphology of the Cu-NPs with reducing time of 160 min. The average diameter of Cu-NPs shown in Figure 4(c) was about 80 nm. The insets located in the lower right corner of Figure 4(a,d) indicated that the Cu-NPs were spherical and well separated in aqueous solution. Figure 4(d) showed that the Cu-NPs were coated with a layer of PVP (with thickness of 2–3 nm) and separated well, suggesting the stabilization effect of PVP for Cu-NPs, which will be discussed later. The lattice fringes shown in Figure 4(b) were visible with a

spacing of about 0.2529 nm, which corresponded to the lattice spacing of the (110) planes of Cu.

The Composition Verification of the Products

XRD is the main characterization methods to identify whether the product was copper, copper oxide, or cuprous oxide. In our work, a more convenient method was used to identify the product. The samples, which were centrifuged at 8000 rpm for 20 min with acetone added in and then washed with alcohol and deionized water three times, were added to silver nitrate solution, and the UV absorption result were shown in Figure 5. The UV-Vis absorption spectra of the solution had an absorption maximum at about 409 nm and this peak was attributed to the surface plasmon peak of silver spherical particles.⁴⁶ The following reaction can be considered:



This experiment evidenced that the product was copper. The copper ions can be reduced to Cu, Cu_2O , or CuO by the redox reaction, depending on the reducing power of reducing agent. It is well known that the CuO and Cu_2O cannot exist at the low pH value solution ($\text{pH} \approx 1$), so the resulting dispersion cannot contain the CuO or Cu_2O , and the most likely product may be the Cu. On the other hand, it indicated that to maintain

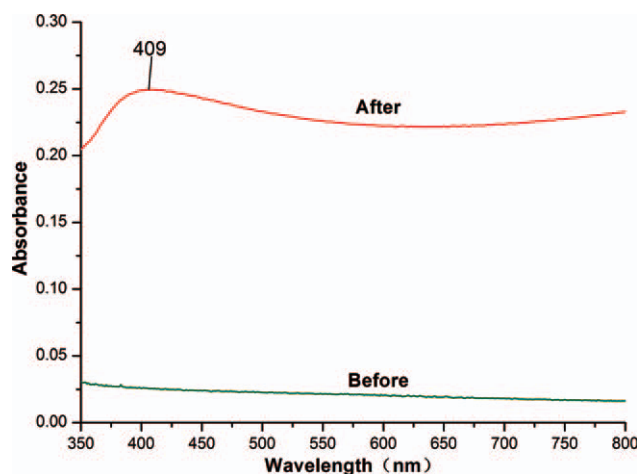


Figure 5. The UV-Vis absorption spectra of the silver nitrate solution before and after added in little Cu-NPs dispersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersions a low pH value had beneficial effects to obtain the Cu-NPs and against the oxidation.

To confirm the crystalline properties of the nanocrystals, the as-synthesized Cu-NPs were further examined using XRD. Figure 6 showed the XRD pattern of the Cu-NPs. The diffraction peaks at $2\theta = 43.5, 50.6,$ and 74.3 were indexed as the [111], [200], and [220] planes of copper with cubic symmetry and matched with reported data (JCPDS 04-0836). No characteristic peaks from impurities, such as $\text{Cu}(\text{OH})_2$, CuO , or Cu_2O were detected, indicating that the products were pure metal Cu. And the background noise was attributable to the PVP adsorbed on the Cu-NPs. This also explained that, due to the surface adsorption of PVP, the Cu-NPs maintained good oxidation resistance.

The Stability of Cu-NPs

The stability of nanoparticle dispersions was an important factor in their applications. PVP was used as capping agent to prevent the agglomeration of nanoparticles. Under ambient conditions, no sign of sedimentation was observed in the PVP-sta-

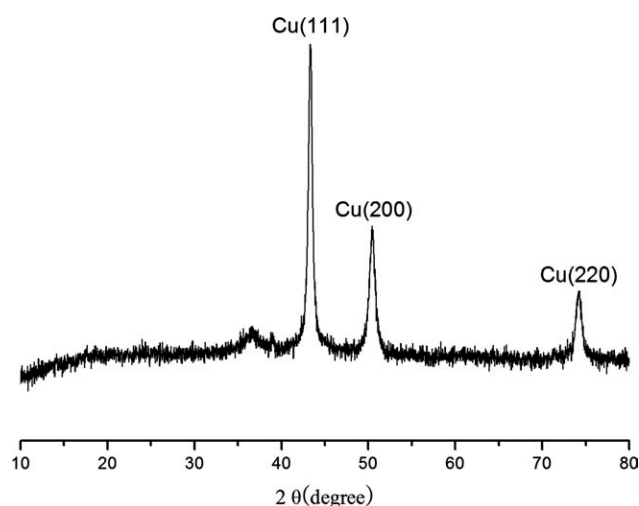


Figure 6. The XRD pattern of prepared Cu-NPs.



Figure 7. The photos of the dispersions (a) before and (b) after 2 months of storage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bilized Cu-NPs dispersions after 2 months storage in a simply test tube, which indicates dispersions was highly stable due to the extreme capping effect of the PVP. The photos of the dispersions before and after the storage are shown in Figure 7. In addition, the precipitate could not be obtained even centrifuged at 8000 rpm for 20 min. Only after adding some acetone, a small amount of precipitate was obtained, as acetone is a poor

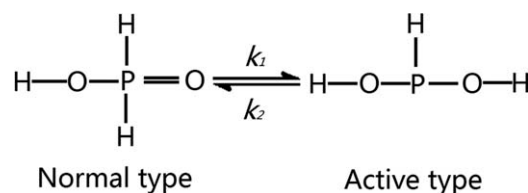


Figure 8. The normal type and active type of sodium hypophosphite.

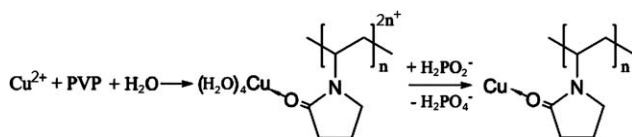


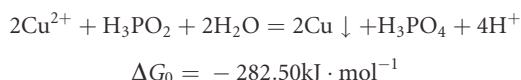
Figure 9. The possible mechanism of PVP on the effective stability of Cu-NPs.

solvent for PVP. For some PVP chelated with Cu-NPs and could not be removed completely, the precipitate can be dispersed completely in alcohol or deionized water again. It indicates that the PVP chelated with Cu-NPs has beneficial effects on the hydrophilic of Cu-NPs.

Possible Mechanism

The above results show that well-dispersed and highly stable Cu-NPs could be obtained using sodium hypophosphite as the reducing agent and PVP as the capping agent under acidic conditions.

The standard electrode potential data of sodium hypophosphite indicated that it has a stronger reducing capacity under alkaline conditions. But the experiment showed that the precipitation of copper hydroxide will be generated when the pH value of solution are greater than 5. So the actual reactant is the water-insoluble copper hydroxide, which leads to the poor dispersibility and stability of final products as a result of the heterogeneous reaction. Under acidic conditions, no copper hydroxide precipitation generated, and the sodium hypophosphite changed from the normal type (not active) to the active type (the metastable structure with two hydroxyl groups),⁴⁷ which make copper sulfate can be reduced to Cu-NPs. The normal type and active type of sodium hypophosphite were shown in Figure 8. The reaction equation under acidic conditions and its change of standard Gibbs free energy are shown as follows:



The protective mechanism of PVP in the copper sulfate-sodium hypophosphite system was generally proposed on the basis of its structural features. PVP was a highly water-soluble compound with strong polarity. PVP has a structure of a polyvinyl skeleton with polar groups. The donated lone pairs of both nitrogen and oxygen atoms in the polar groups of one PVP unit may occupy the hybrid orbitals of copper ions to form a complex compound.

The possible mechanism of PVP on the effective stability of Cu-NPs can be explained from two aspects. One explanation was the capping effect of PVP in the reduction process. The lone pair electrons in the polar groups of PVP can occupy the hybrid orbitals of the copper ion to form a complex compound. The PVP was capped with copper ions as the nanoscopic templates. Through reduction of Cu^{2+} inside nanoscopic templates, small Cu-NPs were easily formed, as illustrated in Figure 9. The other was the dispersion effect of the PVP on the Cu-NPs after the completion of the reduction reaction. As PVP molecules strongly adsorbed on as-prepared metal nanoparticles, they

effectively prevented the aggregation in reducing metal ions.⁴⁸ Consequently, at a higher molecular ratio of PVP and CuSO_4 , more PVP molecules were adsorbed on Cu-NPs surfaces, keeping them from the excessive growth, and leading to form smaller nanoparticles.

CONCLUSION

In summary, we have demonstrated a facile method to synthesize low-cost good dispersed Cu-NPs using sodium hypophosphite as the reducing agent and PVP as the capping agent. The prepared dispersions of Cu-NPs were highly stable and did not show any sign of sedimentation even after storage for 2 months. The highly stable solution of dispersed Cu-NPs can be used as conductive ink for applications such as printed electronics.

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