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Short communication

Anti-oxidative copper nanoparticles and their conductive assembly sintered at room temperature

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ABSTRACT

Copper nanoparticles (CuNPs) can be used as conductive inks for flexible electronics but it suffers low oxidation resistance. After reduction, CuNPs with 40 nm diameter are formed and stabilized by a capping agent. By adding oxygen scavenger, CuNPs become anti-oxidative and can be stored in an ambient condition for at least 10 months. After dilution and centrifugation, the capping agent is removed and CuNP aggregates are obtained. According to field-emission scanning electron microscopy and resistivity, CuNPs are weakly sintered by pressure difference at room temperature and therefore furnish resistivity greater than the typical value of copper. The resistivity of CuNP assemblies is insensitive to the degree of sintering which is increased by annealing.

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1. Introduction

In recent years, the fabrication of flexible circuit board generates great interests due to the growing demand of small, flexible electronics. Polymer-based circuit board is patterning conductive line on the polymer substrate. Polymer is flexible, light-weight, and cheap but suffers poor thermostability and easy degradation. As a result, polymer-based circuit board cannot be manufactured by photolithography which involves high processing temperature and corrosive chemical agents. Instead, printing technology has been used for the fabrication of flexible electronics. Printing technology is printing conductive ink on the polymer substrate to form a designed pattern and then the sintering process is conducted at relatively low temperature. Conductive ink is usually composed of metal nanoparticles and a carrier solvent. Due to high surface energy, metal nanoparticles possess size-dependent properties different from their bulk material. For example, the sintering temperature of nanoparticles is depressed, which allows the use of paper or plastics as flexible substrate [1–5].

Owing to excellent conductivity and high chemical stability of silver nanoparticles, silver ink has been extensively used in disposable electronics such as radio-frequency identification tags. However, the high price of silver limits its industrial applications. Copper has similar resistivity as silver but its price is about 100 times cheaper. As a result, copper ink may be a potential candidate as a substitute for silver ink. Unfortunately, a major problem associated with copper nanoparticles (CuNPs) is their low oxidation resistance in ambient condition. The presence of copper oxide will not only raise sintering temperature but also reduce electrical conductivity of CuNPs. Therefore, how to avoid oxidation of CuNPs which can be sintered at low temperature becomes an important issue.

There are many attempts for the synthesis of CuNPs, such as laser ablation method [6], metal vapor synthesis [7] and chemical reduction method. Recent researches focus mainly on salt reduction method [8], which belongs to the reduction approach, to synthesize CuNPs. In general, those reduction methods involve copper ions reduced by reducing agents in liquid media. The morphology of nanoparticles is easier to control by the salt reduction method. However, CuNPs were found to be easily oxidized in aqueous solutions. Only limited studies have attempted to resolve the oxidation problem [9] and they can be simply divided into two categories. In the core–shell methods, a protective layer is formed on the surface of CuNPs. The protective layer can be inert metal such as silver [10], inorganic materials like

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graphene [11] or silica [12], or organic polymers [13]. Nevertheless, the steps of core–shell synthesis are complicated and the prepared CuNPs have low thermal stability. The electrical conductivity of CuNPs declines subject to heat treatment due to phase separation [14–17]. The other approach is to synthesize CuNPs in the inert gas atmosphere such as glove boxes filled with nitrogen gas [18]. Nonetheless, such synthesized CuNPs cannot be directly processed in ambient condition.

Both aforementioned approaches are based on sequestering CuNPs from oxidizing agents and thus it is difficult to resist oxidation in ambient condition for long periods of time. In this study, a simple and novel method for synthesis of anti-oxidative CuNPs without inert gas protection is developed. CuNPs are easily formed after copper ions reduced by a strong reducing agent in water. By using a relatively weak reducing agent, hydrazine, as oxygen scavenger, the oxygen concentration in aqueous solutions is continually curtailed. As a consequence, the anti-oxidative CuNPs are successfully acquired and can be stored in ambient condition for at least 10 months. Furthermore, a weakly sintered CuNPs aggregate can be obtained by centrifugation at room temperature and its electrical resistivity is close to that of a typical copper foil.
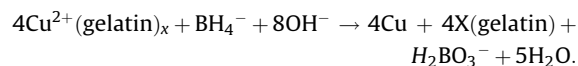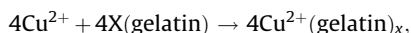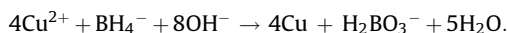
2. Experimental

2.1. Materials

Copper sulfate anhydrous ($CuSO_4$) and sodium hydroxide pellets (NaOH) are purchased from MERCK. Sodium borohydride ($NaBH_4$) is obtained from Alfa Aesar. Gelatin (Type A: from porcine skin, Mw = 50–100k) is the product of Sigma–Aldrich. Hydrazine (N_2H_4) is purchased from Showa Corporation. All chemicals in this work are analytical grade and used as received without further purification.

2.2. Synthesis of anti-oxidative Cu nanoparticles

In the synthesis of CuNPs, copper sulfate ($CuSO_4$) is used as precursor and mixed with gelatin as a capping agent which prevents the agglomeration of CuNPs. 0.3 g of gelatin and 0.02 M $CuSO_4$ dispersed in the deionized water (5 ml). Sodium hydroxide is added to tune the pH value to 12. The color of the solution turns from bluish to purple due to the formation of copper–gelatin complex. Then, 0.1 M of sodium borohydride (5 ml) as a reducing agent is added to the mixture dropwise for the reduction of copper complex. After stirring for 30 min, the color of the mixture becomes dark-red and CuNPs are formed. The reaction mechanism is given as follows:

$$4Cu^{2+} + 4X(gelatin) \rightarrow 4Cu^{2+}(gelatin)_x,$$

$$4Cu^{2+}(gelatin)_x + BH_4^- + 8OH^- \rightarrow 4Cu + 4X(gelatin) + H_2BO_3^- + 5H_2O.$$

Thus, the net reaction is

$$4Cu^{2+} + BH_4^- + 8OH^- \rightarrow 4Cu + H_2BO_3^- + 5H_2O.$$

Finally, 2.5 ml hydrazine of 0.5 M as an oxygen scavenger is added to eliminate oxygen in the CuNP solution. The hydrazine concentration in the final mixture is 0.067 M.

2.3. Characterization

The hydrodynamic diameter of the CuNP dispersion is measured by dynamic light scattering (DLS) carried out on a Malvern Zetasizer Nano-ZS90 with a He–Ne laser (633 nm) and 90° collecting optics. The UV–vis spectra in the range 300–800 nm is recorded by a spectrophotometer (JASCO, V-660). Transmission electron microscope (TEM) images are observed on a JEOL JEM-2000FXII. The samples used for TEM analysis are prepared by placing a few drops of the CuNP dispersion on a copper grid and dried in a vacuum oven at room temperature. The average size of CuNPs is determined from the TEM image containing at least 100 particles. The surface morphology and atomic ratio of the CuNP assemblies are observed via the field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F) equipped with an energy dispersive spectrometer (EDS). Thermogravimetric (TGA) data are collected from 100 to 650 °C at 10 °C/min under dry nitrogen atmosphere by using a Perkin Elmer TGA-7. X-ray diffraction (XRD) measurements are performed using a BRUKER D8AXRD diffractometer with Cu Kα radiation. The powder sample is obtained by diluting the CuNP dispersion with deionized water, centrifugation at 6000 rpm for 30 min (repeat twice), and then vacuum drying at room temperature. The X-ray photoelectron spectroscopy (XPS) of CuNP assemblies is performed using a Sigma Probe spectrometer (Thermo VG Scientific Co. Ltd.) equipped with monochromatic aluminum anode X-ray source (Al Kα 1486.6 eV). The electrical resistivity of CuNP assemblies is measured by a Keithley 2400 source/meter using a four-point probe measurement to avoid the error from contact resistance.

3. Results and discussion

During the formation process of CuNPs, they tend to agglomerate and therefore the size of CuNP grows gradually. In order to obtain CuNPs with size less than 50 nm, capping agents such as polyvinylpyrrolidone are added. In this work, gelatin is added to impart stability of CuNPs due to steric repulsions associated with polymer adsorption onto nanoparticles. In basic solutions, gelatin is deprotonated and the functional group of the side chain is transformed from –COOH to –COO⁻. Because the groups of –COO⁻ and –NH_2 on gelatin can bind with Cu ions, gelatin can be regarded as a multi-ligand and form the copper–gelatin complex in the process of reduction of Cu precursor. After the formation of CuNPs, the adsorption of gelatin on the surfaces of nanoparticles prevents further aggregation and helps the control of particle size.

However, only a small range of gelatin concentration is able to yield CuNPs of 50 nm in size. Fig. 1 shows the effect of gelatin concentration on the size of CuNPs determined by DLS. The
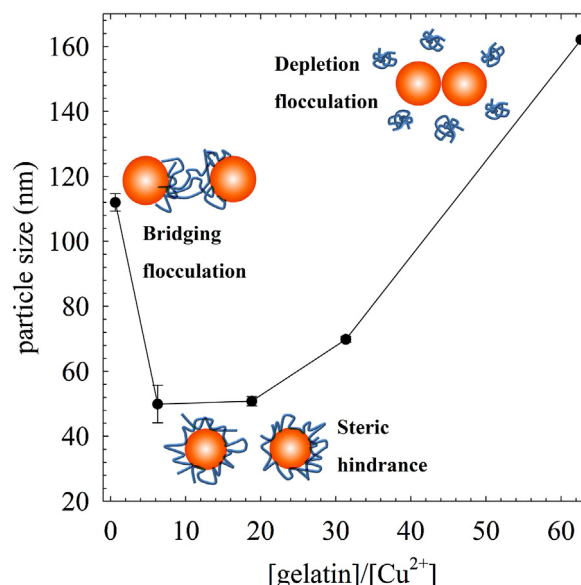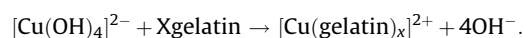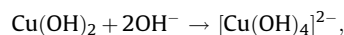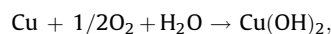

Fig. 1. The effect of gelatin concentration on the size of CuNPs.

smallest average particle diameter is about 50 nm as the weight ratio of gelatin to copper (II) ion is in the range of 6–20. When the gelatin concentration is too low, the mechanism of steric hindrance fails and CuNPs aggregate because of bridging flocculation. It is a consequence of the adsorption of the segments of individual polymer onto the surface of more than one particle. On the other hand, as the gelatin concentration is too high, CuNPs also cluster together although the surface of CuNP is fully covered with gelatin. In fact, depletion-induced aggregation takes place due to an increase in osmotic pressure by gelatin [19,20].

In general, CuNPs show a characteristic absorption peak (shoulder) at 570–580 nm on UV–vis spectrum because of surface plasmon resonance [21]. If CuNPs are oxidized in basic condition and become tetrahydroxycuprate, $[Cu(OH)_4]^{2-}_{(aq)}$, the absorption peak will disappear. In the presence of gelatin, the ligands in $[Cu(OH)_4]^{2-}$ will be replaced to form $Cu^{2+}(gelatin)_x$, which displays a broad absorption peak around 525 nm. As a result, the stability of CuNPs against oxidation can be examined by UV–vis spectrum. In the absence of oxygen scavenger, the typical variation of UV–vis spectrum associated with the formation and disappearance of CuNPs is illustrated in Fig. 2. The spectrum corresponding to 4 h after copper reduction clearly demonstrate the existence of CuNPs. The fact that the intensity of absorption peak of 6 h grows indicates more CuNPs being formed. However, after 19 h, the absorption intensity drops significantly and becomes less than that of 4 h. This consequence reveals the oxidation of CuNPs. Eventually, CuNPs vanish and the complexes of copper–gelatin are formed, as shown in the inset of Fig. 2. The oxidation of CuNPs can be further verified by the XRD analysis. The oxidized CuNPs dispersion stored for 19 h are diluted with deionized water and then separated by centrifugation. The precipitates are analyzed by XRD and the pattern demonstrates the formation of copper oxide in the absence of hydrazine, as shown in Fig. 3.

CuNPs are easily oxidized in the aqueous solution and the reaction mechanism in basic condition is given as follows:

$$Cu + 1/2 O_2 + H_2O \rightarrow Cu(OH)_2,$$

$$Cu(OH)_2 + 2OH^- \rightarrow [Cu(OH)_4]^{2-},$$

$$[Cu(OH)_4]^{2-} + X gelatin \rightarrow [Cu(gelatin)_x]^{2+} + 4OH^-.$$

Evidently, oxygen is required for CuNPs oxidation. In other words, oxidation cannot proceed in the absence of oxygen. If oxygen in
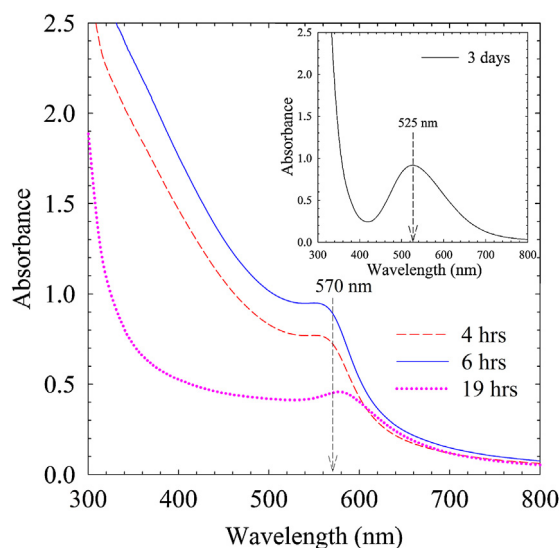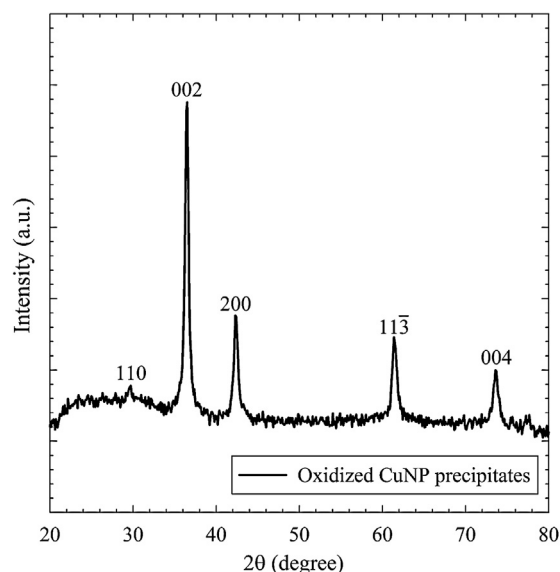

Fig. 3. The XRD pattern of oxidized CuNP precipitates.

CuNP dispersions is removed, then anti-oxidative CuNPs are anticipated to be obtained. In addition to the inert gas atmosphere, the oxygen-absence environment can be achieved by the addition of oxygen scavenger. In general, reducing agents such as hydrazine and ascorbic acid are able to scavenge oxygen in aqueous solutions. By addition of N_2H_4, we are able to acquire CuNPs resisting oxidation for at least 10 months. Fig. 4 displays the time variation of UV–vis spectrum of CuNPs in the presence of N_2H_4. As time progresses, the intensity of the spectrum grows and eventually becomes time-invariant. The peak positions remain the same. Moreover, the color of the CuNP dispersion is always dark-red, instead of purple color associated with copper–gelatin complex due to oxidation. These observations reveal that the concentration of CuNPs increases initially with time, reaches a constant, and remains unchanged because further oxidation is inhibited by oxygen removal. Further evidence on anti-oxidative CuNPs can be provided by transmission electron microscopy. Fig. 5(a) shows an image of CuNPs with distributed sizes and the mean diameter is about 40 nm, which is consistent with the result of DLS. The sample

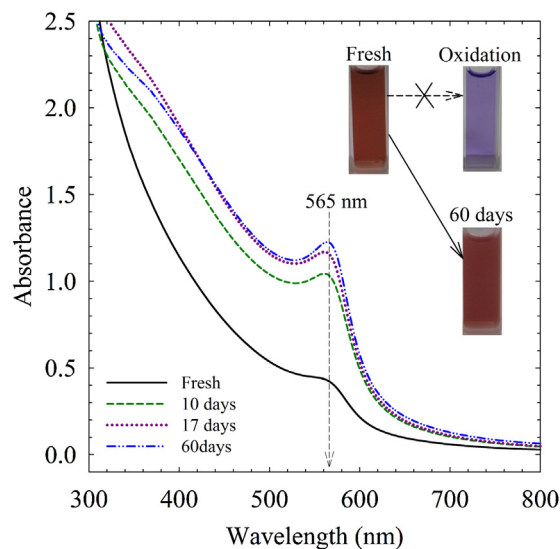Fig. 2. The variation of UV–vis spectrum with time for CuNPs without oxygen scavenger.

Fig. 4. The variation of UV–vis spectrum with time for CuNPs with hydrazine as the oxygen scavenger. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)
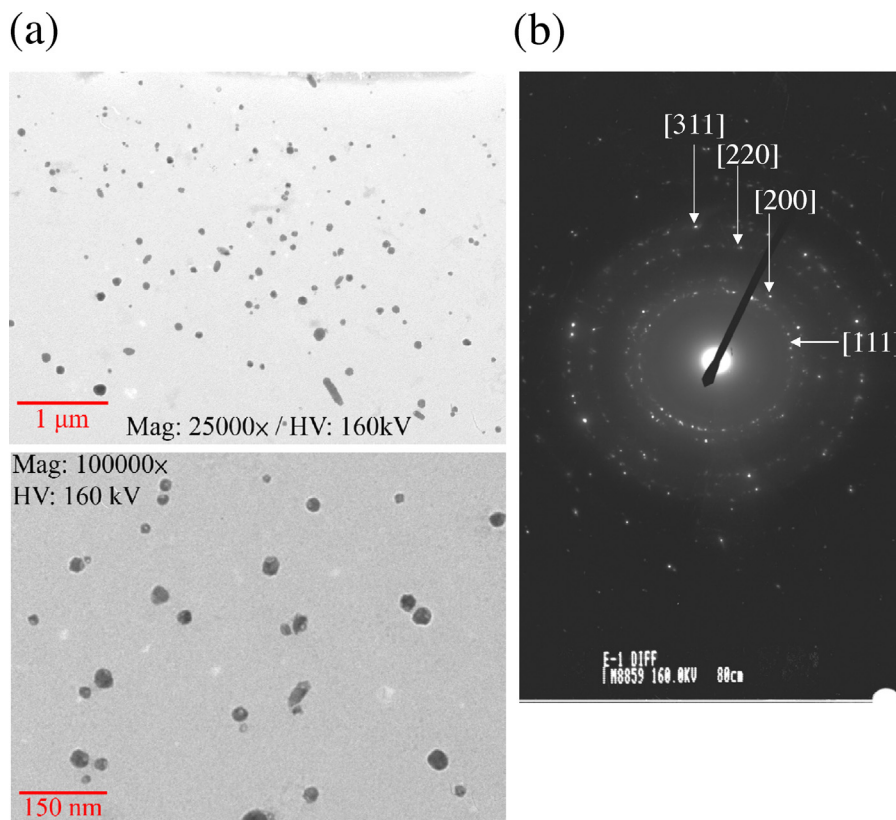
(a)

(b)

Fig. 5. (a) The TEM image and (b) the selected-area electron diffraction pattern of CuNPs.

has been stored in the ambient condition for 2 months. The electron diffraction ring pattern is also demonstrated in Fig. 5(b) and the profile is consistent with that of copper.

In order to determine the electrical resistivity of weakly sintered CuNP assembly, the dispersion of anti-oxidative CuNPs is centrifuged at room temperature. However, the presence of

capping agent prevents aggregation and further sintering during centrifugation [22]. Therefore, the CuNP dispersion is diluted by hydrazine aqueous solution and then CuNPs settle out of the fluid by centrifugation. The dark-red sediment of CuNPs can be redispersed by sonication in $N_2H_{4(aq)}$ but becomes weakly sintered after centrifugation and drying. The sheet precipitated at the bottom of the centrifugal tube is shinny and can be picked up by tweezers, as illustrated in Fig. 6. The residue of gelatin in the assembly of CuNPs is analyzed by thermogravimetric analysis and only 3.5 wt% is left, as shown in Fig. 7. Note that the initial weight ratio of gelatin to copper sulfate is about 19:1. The feature of the
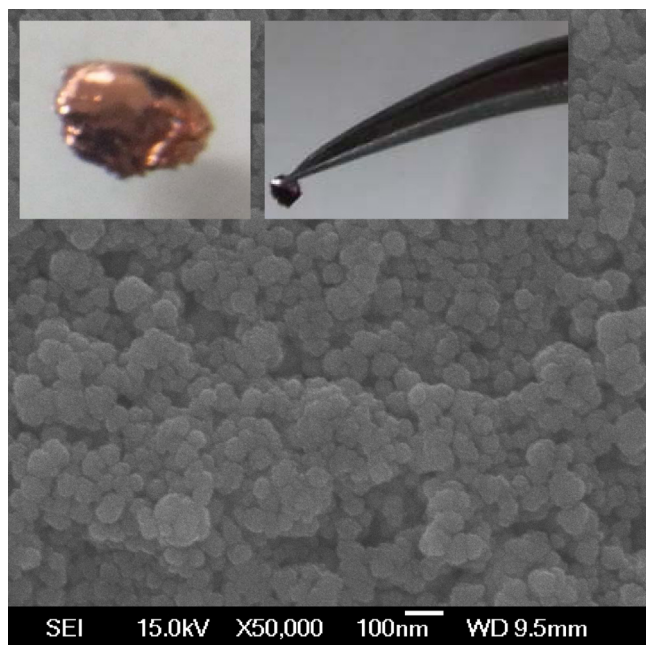

Fig. 6. The FE-SEM image of a CuNP assembly. The scale bar is 100 nm. The upper insets show the metallic shine of the CuNP assembly which can be picked up by tweezers.
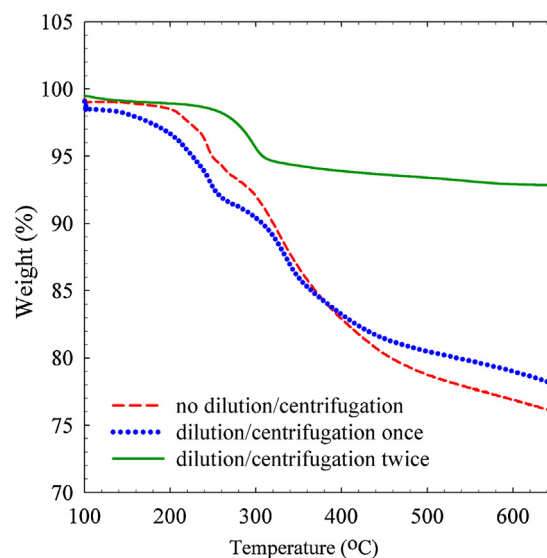

Fig. 7. The TGA curves of CuNP assemblies obtained by different treatments.
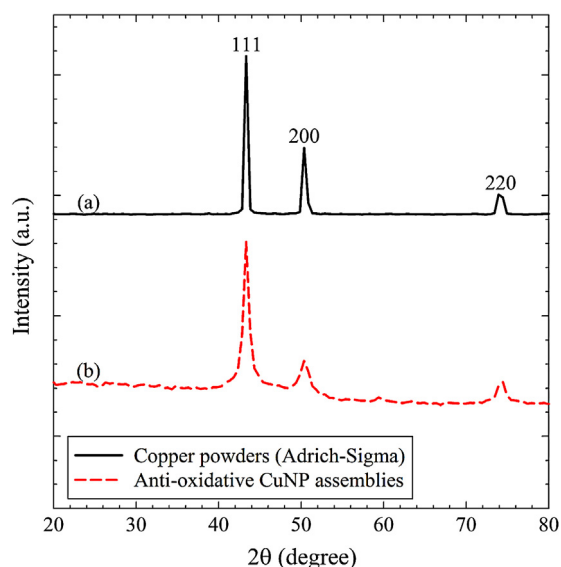
Fig. 8. The XRD patterns of (a) copper powders (Aldrich–Sigma) and (b) CuNP assemblies.

Fig. 9. XPS Cu 2p$_{3/2}$ spectra of anti-oxidative CuNP assembly.

Table 1
The elemental distribution of CuNP assembly obtained by EDS.

Times of dilution/centrifugation	Elements (wt%)			
	Cu	O	N	C
0	12.67	46.71	10.67	20.32
1	59.72	18.88	4.07	13.05
2	84.41	5.97	3.03	6.22

CuNP assembly is further examined by field-emission scanning electron microscopy (FE-SEM). As shown in Fig. 6, the shape of CuNPs is clearly seen and they are densely packed. According to the aforementioned observations, the interactions among CuNPs are not only van der Waals attractions but also metallic bonds. That is, they provide the CuNP assembly to resist the mechanical stress. The metallic bonds correspond to weakly sintering driven by pressure difference associated with centrifugation.

The self-assembly of CuNPs (precipitated nanoparticles) in the solution after centrifugation is still anti-oxidative because of the presence of the oxygen scavenger, hydrazine. The XRD analysis has been performed and the patterns show that the dried CuNP assemblies are copper by comparing them with those of fresh copper powder purchased from Aldrich–Sigma. The result is given in Fig. 8. Our statement can be verified by X-ray photoelectron spectroscopy (XPS) spectrum of Cu 2p$_{3/2}$. As shown in Fig. 9, the low Cu 2p$_{3/2}$ binding energy (about 933.2 eV) is a characteristic of the copper species and other peak due to CuO is absent. It is indicative of the absence of surface oxide layer of CuO. The elemental distribution of CuNP assembly has also been analyzed by EDS and the main component is copper, as shown in Table 1. The weight ratio of oxygen atom is about 6% and may come from the residual gelatin. This outcome is consistent with the result of TGA.
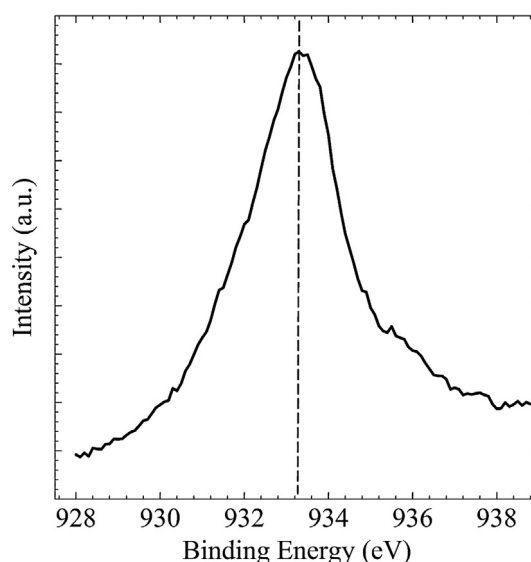
Note that in the absence of hydrazine, the precipitate of oxidized nanoparticles is difficult to be sintered at room temperature. Another evidence for the CuNP assembly remaining anti-oxidative is manifested by its electrical conductivity. In general, the resistance of the aggregate of CuO particles is too high to be determined by typical measurements.

The electrical property of the CuNP assembly is measured by two-point and four-point probe measurement. The resistivity of the CuNP assembly is about 1.5×10^{-3} Ω cm which is slightly less than the previously reported values [22,23]. Note that our CuNP assembly is weakly sintered at room temperature without subject to high temperature annealing treatment which has been employed by previous studies. Therefore, our CuNPs dispersion is suitable for conductive copper inks. In addition, we are unable to obtain the resistivity of micron-sized copper powders which is not
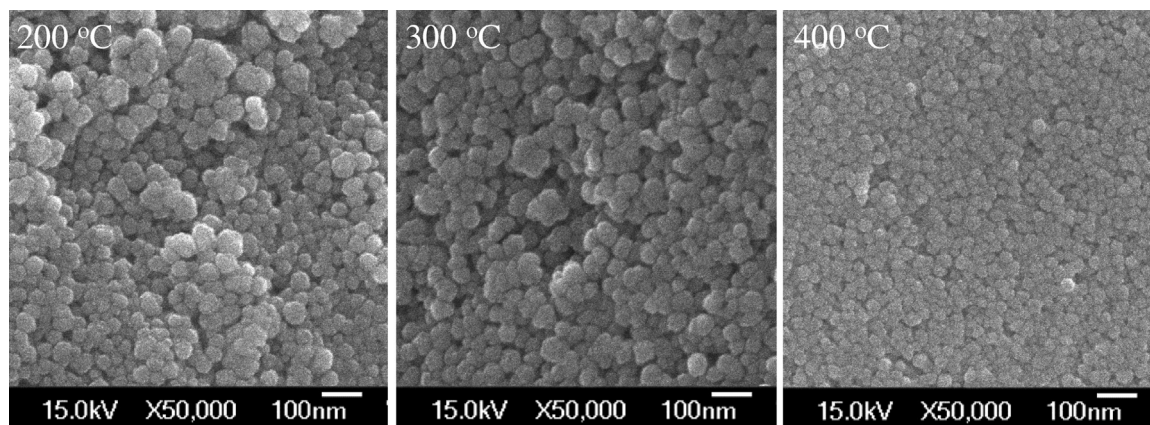

Fig. 10. The FE-SEM images of CuNP assemblies annealed at 200, 300 and 400 °C.

Table 2
The resistivities of CuNP assemblies annealed at different temperatures.

Annealing temperature (°C)	Electrical resistivity (Ω cm)
Room temperature	1.5×10^{-3}
200	2.46×10^{-3}
300	1.67×10^{-3}
400	1.91×10^{-3}

sintered. As a result, sintered CuNP assembly is required for electrical conduction. The influence of the degree of sintering on the electrical resistivity is further explored. CuNP assemblies are subject to annealing process at temperature of 200, 300 and 400 °C in nitrogen atmosphere, respectively. Fig. 10 displays the FE-SEM images of surfaces morphology after heat treatment. As the annealing temperature is increased, the electric resistivity shows no significant change, as shown in Table 2. This consequence reveals that the resistivity of the CuNP assembly is insensitive to the degree of sintering.

4. Conclusion

The CuNPs have been synthesized by the salt reduction method and are stabilized by the capping agent (gelatin). By using a relatively weak reducing agent (hydrazine) as oxygen scavenger, the anti-oxidative CuNPs are obtained. The adsorption of gelatin on the surfaces of CuNPs prevents further aggregation and helps the control of particle size. The size of CuNPs determined by DLS is about 50 nm. Moreover, the oxygen concentration in aqueous solutions is continually curtailed by hydrazine. According to the UV–vis spectrum and TEM electron diffraction ring pattern, the anti-oxidative CuNPs dispersion can be stably stored in ambient condition for at least 10 months.

The CuNP assembly after centrifugation cannot be redispersed by sonication and can be picked up by tweezers. This result indicates the presence of metallic bonds, which correspond to weakly sintering driven by pressure difference associated with centrifugation at room temperature. The in-depth information on the presence of surface oxide layer is analyzed by XPS and the absence of CuO is demonstrated. Furthermore, the CuNP assembly weakly sintered at room temperature shows a densely packed morphology of CuNPs but exhibits electrical resistivity slightly higher than the reported values.

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