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

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.
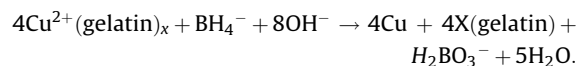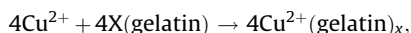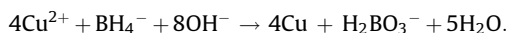
2. Experimental

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
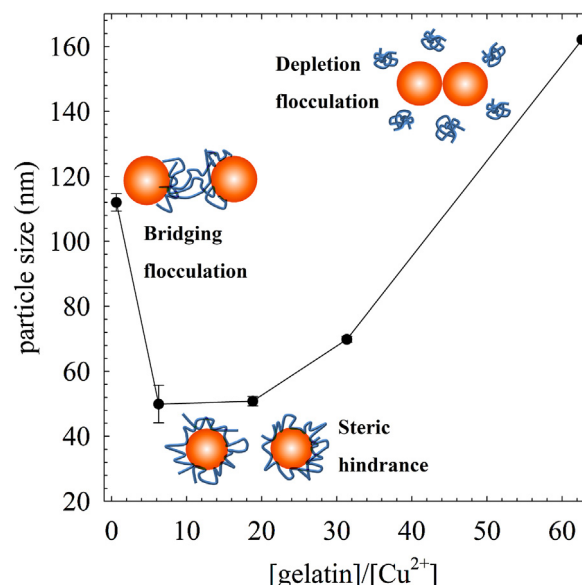

Fig. 1. The effect of gelatin concentration on the size of CuNPs.