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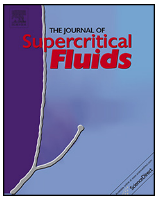

Continuous supercritical hydrothermal synthesis of dispersible zero-valent copper nanoparticles for ink applications in printed electronics

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ABSTRACT

Surface-modified zero-valent copper nanoparticles (CuNPs) are of interest as conductive inks for applications in printed electronics. In this work, we report on the synthesis, stability and characterization of CuNPs formed with a continuous supercritical hydrothermal synthesis method. The precursor, copper formate, was fed as an aqueous solution with polyvinylpyrrolidone (PVP) surface modifier and mixed with an aqueous water and formic acid stream to have reaction conditions of 400 °C, 30 MPa and 1.1 s mean residence time. The reaction pathway seemed to proceed step-wise as the hydrolysis of copper formate, followed by dehydration to oxide products and subsequent reduction by hydrogen derived from precursor and formic acid decomposition. The formed surface-modified zero-valent CuNPs had particle sizes of ca. 18 nm, were spherical in shape and contained no oxide contaminants. The formed CuNPs were found to exhibit long-term (>1 year) stability in ethanol as evaluated by shifts in the surface plasmon resonance band of product solutions. Conductive films (0.33 μm thickness) prepared with the CuNPs had a resistivity of 16 $\mu\Omega$ cm. The methods reported in this work show promise for producing conductive inks for use in practical printed electronics.

1. Introduction

Printed electronics are being explored world-wide due to their potential for use in functional low-cost devices that are flexible, stretchable, lightweight, and thin [1–3]. Printed electronics form an electronic line in two steps: (i) printing of conductive inks onto a substrate, and (ii) sintering of the substrate to form a permanent image [4–6]. The two step process has the possibility of being more convenient and cost effective for advanced electronics than present multi-step methods [7].

Conductive inks being proposed for printed electronics consist of fine metallic particles that are surface-modified by a stabilizer and dispersed homogeneously into a solvent [3,4,8]. In the use of the conductive inks, gold [9], silver [10,11] and copper [12–15] nanoparticles have been studied by many researchers, with silver nanoparticles being popular since it exhibits the lowest electrical resistivity among these metals and it is stable under oxidizing atmospheres. However, silver nanoparticles inks are not suitable for line and films of electronic devices because of their high cost and the electrochemical migration of silver that tends to lead to dendrite growth and short circuits [16,17]. On the other hand, it can be considered that copper nanoparticles (CuNPs) have good potential for printed electronics, since copper has a much lower cost than silver and its electrochemical migration rarely takes place [6] even though copper has almost the same electrical resistivity as silver.

However, one problem with CuNPs is that they readily oxidize, which leads to their aggregation, and moreover, the rate of oxidation of CuNPs at ambient conditions in air or in solvents is much higher than that of silver nanoparticles [15,18,19]. The presence of a surface oxide layer on CuNPs causes an increase in the sintering temperature and a decrease in the electrical conductivity [20]. Another problem with CuNPs is that blockage of ink-jet printing nozzles tends to occur possibly due to the lack of dispersion of CuNPs in the ink. Therefore, storage lifetime, defined as long-term oxidation and dispersion stability, is an important property for practical use and acceptance in industry. In some studies on CuNPs for conductive inks, one useful method for protecting the

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surface of CuNPs is surface modification through the coordination bond of an alkyl carboxylic acid [12,14], alkyl amine [14,21,22] or polymer [20,23–25], to the CuNPs so that oxidation and aggregation are inhibited.

CuNPs have been synthesized by various methods, such as sol–gel [26], electrolysis [27], reverse-micelle [28], thermal decomposition [29–31] and polyol [25,32,33] techniques. In these methods, an organic solvent is used with a strong reducing agent such as hydrazine, both of which are of concern regarding their environmental impact. Large-scale production is thought to be difficult due to the usual batch process nature of these methods. Therefore, continuous supercritical hydrothermal synthesis probably has good potential as an alternative method, because water can be used as an environmentally benign solvent and the short reaction time could allow efficient synthesis.

One method for producing CuNPs continuously is based on the chelation of Cu with bis(hexafluoroacetylacetonate) in supercritical CO_2 with ethanol co-solvent [34]. In that method, ethanol co-solvent in the supercritical CO_2 phase is used to dissolve the chelate precursor before its thermal decomposition after spraying onto a hot surface [34]. The method can be used to produce zero-valent CuNPs but requires the use and destruction of fluorinated compounds to produce CuNPs and those particles will still require surface modification for use as conductive inks [35].

Particle synthesis consists of nucleation and particle growth [36–39]. Supercritical hydrothermal synthesis allows rapid nucleation and limited particle growth since the method heats the material precursor directly by mixing with water at high temperatures [40,41]. However, there seem to be few studies on the formation of zero-valent CuNPs under hydrothermal conditions most likely due to the ease at which CuNPs oxidize. Ziegler et al. produced CuNPs using 1-hexanethiol as surface modifier and reducing agent at supercritical water conditions with a batch-typed reactor and succeeded in CuNPs having a dispersion stability [42]. However, large-scale synthesis with this method would need to consider the corrosion caused by sulfur in the electrical substrate due to use of thiol. Arita et al. [43] studied the synthesis of metal (Ag, Ni, Pd, Fe and Cu) particles with batch methods using metal formate and formic acid additives that decompose to hydrogen (H_2) at reaction conditions. They reported zero-valent silver and copper could be synthesized with the supercritical hydrothermal synthesis method. Therefore, in this work, we adopted formic acid as a reducing agent in the study of production of CuNPs with a continuous supercritical hydrothermal method. Considering the above technical challenges, the objectives of this work can be stated as: (i) to synthesize zero-valent CuNPs continuously with the supercritical hydrothermal synthesis method, (ii) to determine the stability of surface-modified CuNPs in several solvents and (iii) to assess the feasibility of the dispersed CuNPs as conductive inks.

2. Experimental

2.1. Materials

Copper formate tetrahydrate (Wako Pure Chemicals, 98.0%) was used as a precursor of Cu. Polyvinylpyrrolidone (PVP) (M_w = 40,000; Wako Pure Chemicals) was used as a surface modifier, formic acid (HCOOH) (Wako Pure Chemicals, 98.0%) was used as a reducing agent and ethanol (Wako Pure Chemicals, 99.5%) was used as the dispersion solvent for the CuNPs. Methanol (Wako Pure Chemicals, 99.7%) and acetone (Wako Pure Chemicals, 99.5%) were used to wash the particles. In procedures for freeze-drying, tert-butyl alcohol (Wako Pure Chemicals, 99.0%) was used as a solvent for the CuNPs.

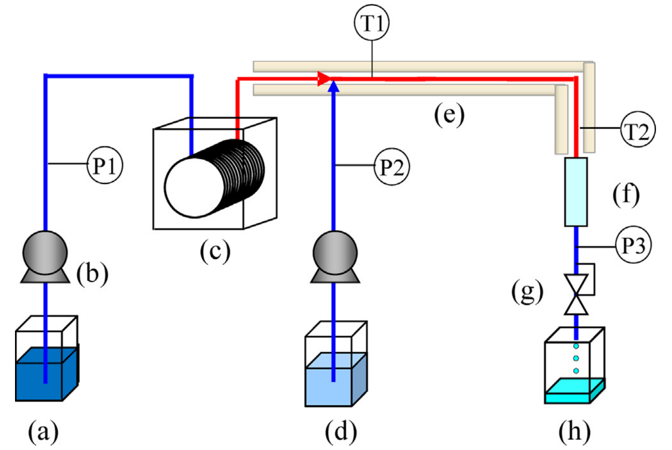

Fig. 1. Schematic diagram of continuous flow apparatus for producing surface-modified copper nanoparticles (CuNPs). (a) Feed solution (water or HCOOH *aq*), (b) Pump, (c) Preheater, (d) Precursor solution ($Cu(HCOO)_2$ + PVP + water), (e) Reaction tube, (f) Cooler, (g) Back-pressure regulator and (h) Product solution. T1, T2: thermocouples; P1, P2, P3: pressure sensors.

2.2. Experiment

Reactions were conducted using a continuous flow apparatus (Fig. 1). The reactor consisted of a 1/8 in. SUS316 tube (JIS, inner diameter, 1.78 mm). Copper formate tetrahydrate was dissolved in distilled water together with PVP to prepare a precursor solution. Distilled water or a formic acid aqueous solution was used as a feed solution. The precursor solution was fed by a high-pressure pump, and mixed with a feed solution that was pre-heated to a given temperature by an electric furnace. A mixture of the precursor solution and the feed solution was allowed to flow through the reactor, and after reaction was brought to atmospheric temperature and pressure with a cooler and a back pressure regulator. The products were separated from the supernatant by adding excessive amounts of acetone that was followed by centrifugation. The resulting sediments were redispersed with water, ethanol, or tert-butyl alcohol using ultrasonic irradiation. The products in water and ethanol were stored in capped glass bottles, and only products in ethanol were considered for assessment as CuNPs inks due to oxidation of some of the products formed as described later. The products were dispersed in tert-butyl alcohol and freeze-dried overnight to obtain powder products.

A summary of the reaction conditions studied and the product crystallite size, average particle size, major morphology and the CuNPs surface plasmon resonance (SPR) are given in Table 1. In Table 1, runs 1–3 and runs 4–6 were used to examine the effect of temperature and formic acid on the reaction; runs 6–8 were used to evaluate the effect of the concentration of the formic acid reducing agent on the reaction; runs 6, 9 and 10 were used to study the effect of precursor concentration; runs 6 and 12 were used to study the effect of flow HCOOH *aq*./precursor on the products; and runs 11–13 were used to examine the effect of reaction time on the particles formed.

2.3. Analyses

The crystal structure of the products was determined with an X-ray diffractometer (XRD), Rigaku RINT 2000. The crystallite sizes (D_{XRD}) were calculated from the peak broadening of the most intense XRD peak using the Scherrer formula, $D_{XRD} = 0.9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (CuKα, 1.54056 Å) used and β is the half-width of the peak. The confirmation of CuNPs formation and evaluation of their oxidation in various dispersion solvents were