Journal of Colloid and Interface Science 359 (2011) 19–23

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Synthesis of pure colloidal silver nanoparticles with high electroconductivity for printed electronic circuits: The effect of amines on their formation in aqueous media

Jun Natsuki *, Takao Abe

Faculty of Fiber & Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

ARTICLE INFO

Article history:
Received 9 November 2010
Accepted 23 March 2011
Available online 27 March 2011

Keywords:
Silver nanoparticle
Electronic circuit
Digital fabrication
Inkjet ink
Electroconductivity
Amine

ABSTRACT

This paper describes a practical and convenient method to prepare stable colloidal silver nanoparticles for use in printed electronic circuits. The method uses a dispersant and two kinds of reducing agents including 2-(dimethylamino) ethanol (DMAE), which play important roles in the reduction of silver ions in an aqueous medium. The effect of DMAE and dispersant, as well as the factors affecting particle size and morphology are investigated. In the formation of the silver nanoparticles, reduction occurs rapidly at room temperature and the silver particles can be separated easily from the mixture in a short time. In addition, organic solvents are not used. Pure, small and relatively uniform particles with a diameter less than 10 nm can be obtained that exhibit high electroconductivity. The silver nanoparticles are stable, and can be isolated as a dried powder that can be fully redispersed in deionized water. This method of producing colloidal silver nanoparticles will find practical use in electronics applications.

1. Introduction

Because an inkjet printhead can place an ink droplet of a fixed volume at a decided place, inkjet printing technology has attracted much attention to application in digital fabrication of electronic circuits. Inkjet printing technology has a number of benefits: (1) Fine images are printed evenly on a curved surface. (2) Printing media of various sizes can be used. (3) Complicated color images are easily printed without the prepress plates required in conventional printing. (4) High throughput is possible. Because of these advantages, it has been used to produce displays, devices and 3D printing.

Inkjet technology has been used to produce flexible electronic circuits at low cost, and many studies regarding this application have been reported in recent years [1–3]. To fabricate flexible electronic displays *via* inkjet printing, it is necessary to develop suitable inks. We have an interest in inkjet inks containing dispersions of nano-sized metal particles that are useful for producing electronic circuits because of the uniformity of the small metal particles dispersed in the inks [4–6]. Interest in the synthesis and properties of colloidal metal nanoparticles has been increasing because of their unusual optical, physical and chemical properties, which differ from the bulk properties and show promise for application as catalysts and semiconductors. Metal particles with diameters of 1–10 nm are most attractive for theoretical and practical reasons [7–9].

Inks that are a dispersion of nano-sized metal particles have a number of merits: it is possible to print an electronic circuit and then sinter at relatively low temperature because of the small size of the metal particles; a fine pitch can be obtained easily; metal nanoparticle inks are stable; with such inks fabrication of electronic circuits can be achieved readily at low resistivity. Nano-sized metal particles have been used widely in various fields including catalysis and photonics. In particular, silver nanoparticles are used widely in the electronics industry as thick film conductors in integrated circuits because of their low resistivity.

It is known that conventional processes usually produce powders with large grains of irregular shape that tend to aggregate. This kind of powder is difficult to use in various fields. For example, the nozzles of an inkjet printer clog up when metal powders or large-sized particles are dispersed in inks. However, by introducing colloid and interface science into the synthetic process, it becomes possible to prepare uniform colloidal nano-sized particles covered with dispersant. In addition, the dispersant can prevent the silver nanoparticles from aggregating.

Abbreviations: XRD, X-ray diffraction; TEM, Transmission electron microscopy; EDS, Energy dispersive X-ray spectroscopy; SEM, Scanning electron microscopy; FT-IR, Fourier Transform infrared absorption spectroscopy; PVP, Polyvinylpyrrolidone; $AgNO_3$, Silver nitrate; Na_3Ct, Trisodium 2-hydroxypropane-1,2,3-tricarboxylate; DMAE, 2-(Dimethylamino) ethanol; $NaBH_4$, Sodium tetrahydridoborate.

* Corresponding author. Fax: +81 0268 21 5610.
E-mail address: jnatsu@shinshu-u.ac.jp (J. Natsuki).

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.03.079

Both chemical and physical methods have been used to prepare metal nanoparticles. Chemical reduction is the most common method because of its convenience and simple equipment. Control over the growth of metal nanoparticles is required to obtain nanoparticles of small size with a spherical shape and narrow distribution in diameter. It is well known that silver nanoparticles can be produced by chemical reaction at low cost and in high yield. Various reducing agents (e.g., sodium tetrahydridoborate, hydrazine, ethanol, ethylene glycol, and ascorbic acid), dispersant (e.g., polyvinylpyrrolidone (PVP), and polyethylene oxide) have been used in nanoparticle preparation [10–21]. For example, Radziuk et al. prepared silver nanoparticles by reduction of silver nitrate in an excess of aqueous $NaBH_4$, obtaining nanoparticles with a diameter of 20 nm [16]. Tan et al. synthesized silver nanoparticles by reduction of silver nitrate using potassium bitartrate at 100 °C for 2 h [17]. Hsu et al. synthesized silver nanoparticles using formaldehyde [18]. However, these reactions possess many problems: a large volume of organic solvent or expensive reagents are needed; the reduction process proceeds at relatively high temperature; and the complete separation of silver particles is not easy because of the presence of other compounds in the reaction mixture.

From an industrial point of view, it is necessary to develop simple and low-cost processes to produce large quantities of silver nanoparticles. In this study, we have attempted to find a practical and convenient method to prepare silver nanoparticles without the use of organic solvent and that can be readily separated from the reaction mixture. Silver nanoparticles were produced using trisodium 2-hydroxypropane-1,2,3-tricarboxylate combined with 2-(dimethylamino) ethanol (DMAE) as a reducing agent and PVP as a dispersant. The reaction can be performed at room temperature in a short time with cheap reductants, which contribute to cost reduction and easy operation. Small, pure, uniform silver nanoparticles with diameters (<10 nm) can be obtained that exhibit high electroconductivity. These advantages will bring about promising application to industrial manufacture of stable colloids of silver nanoparticles, which are applicable in digital fabrication of electronic circuits.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$), trisodium 2-hydroxypropane-1,2,3-tricarboxylate hydrate (Na_3Ct), and DMAE were obtained from Wako Pure Chemicals Co. PVP (molecular weight ~10,000) was obtained from Tokyo Kasei Co., Ltd. Deionized water was used throughout the experiments.

2.2. Preparation of silver nanoparticles

PVP (1.0 g) was dissolved in deionized water (20 ml) by stirring for 10 min at room temperature. $AgNO_3$ (0.50 g, 2.94 mmol) was added and the solution was stirred for 10 min to allow the $AgNO_3$ to dissolve. An aqueous solution of Na_3Ct (0.88 g, 2.94 mmol) in deionized water (20 ml) was added dropwise using a micro-pump. After all of the Na_3Ct solution had been added, an aqueous solution of DMAE (0.027 g, 0.294 mmol) in deionized water (0.5 ml) was added to the reaction mixture. The mixture was then stirred at room temperature for one hour. The color of the solution gradually changed from white to pale brown. The silver particles were separated from the solution by centrifugation (5000 rpm), washed twice with deionized water (20 ml), and then redispersed in deionized water (10 ml).

The same reaction procedure described above was used to prepare other nanoparticles by varying the amounts of reactants.

To measure volume resistivity, a suspension of silver nanoparticles was coated on a polyimide film. The samples were then sintered in an oven for 1 h at 200, 250 or 300 °C before testing.

2.3. Characterization

UV–Visible spectra of the silver nanoparticles were obtained with a Hitachi U-4100 UV–Vis spectrophotometer as suspensions in an optical cell. Transmission electron microscopy (TEM) images of the silver nanoparticles were obtained on a JEOL JEM 2010 TEM operating at 200 kV. The distribution of the diameter of the silver particles was measured using a Zetasizer Nano-Series (Malvern Instruments). Energy-dispersive spectroscopy (EDS) analysis was carried out on a Hitachi S-5000 scanning electron microscope (SEM) equipped with an EDS instrument using a dried powder sample of silver nanoparticles. X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX-IIIV XRD using Cu Kα radiation. Fourier transform infrared (FT-IR) analysis was performed using an IR Prestige-21 spectrometer (Shimadzu), using the attenuated total reflection method. The volume resistivity was measured with a Loresta-GP MCP-T610 resistivity meter (Mitsubishi Chemical Analytech Co., Ltd.) using a four-probe method.

3. Results and discussion

3.1. Optical properties of the prepared silver nanoparticles

Fig. 1 shows a UV–Visible absorption spectrum of the silver nanoparticles. A characteristic absorption band with a peak at λ_{max} = 420–430 nm is observed for the silver nanoparticles, which is consistent with literature values [19].

The results of EDS analysis are presented in Fig. 2. The intense peak at around 3 keV is characteristic of silver nanoparticles and is similar to literature values [18]. No impurities are observed besides small amounts of carbon and oxygen, which indicates that the reagents used have not remained. Because the chemicals used in this study are water-soluble, the final product, which is insoluble in water, can be separated easily from the reaction mixture.

A TEM image of the silver nanoparticles is shown in Fig. 3. It is clear that the silver nanoparticles are spherical. Although a few larger particles (about 0.8%) exist, the diameter of the majority of particles (99.2%) is less than 10 nm. The distribution of the diameters of the silver nanoparticles is shown in Fig. S1. The measured samples contain 99.2% silver nanoparticles within a size range of 2.70–4.85 nm, indicating that the silver nanoparticles show a narrow distribution of diameters except for a few larger particles.

An XRD pattern of the particles is shown in Fig. S2. The reflection peaks were indexed as the fcc (1 1 1), (2 0 0), (2 2 0), and

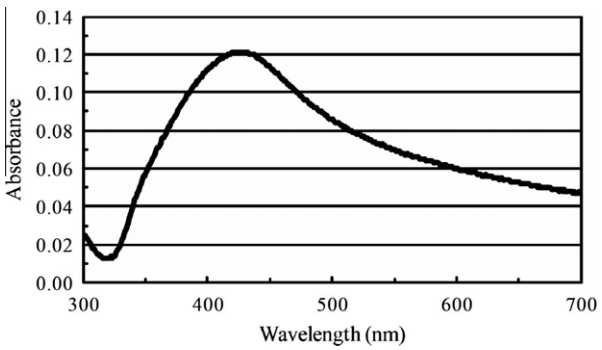

Fig. 1. UV–Vis absorption spectrum of a suspension of silver nanoparticles.