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Properties of polyacrylic acid-coated silver nanoparticle ink for inkjet printing conductive tracks on paper with high conductivity

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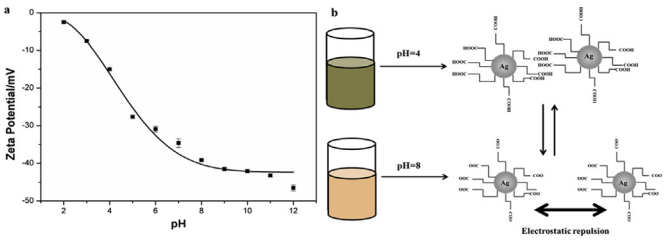
HIGHLIGHTS

- An ink from silver nanoparticles coated with polyacrylic acid was prepared.
- The ink was used for inkjet-printed tracks at varying printing parameters.
- The conductivity of printed tracks sintered at 150 °C increased to 2.1×10^7 S/m.
- Mechanism for dispersion and aggregation of the nanoparticles in ink is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles with a mean diameter of approximately 30 nm were synthesized by reduction of silver nitrate with triethanolamine in the presence of polyacrylic acid. Silver nanoparticle-based ink was prepared by dispersing silver nanoparticles into a mixture of water and ethylene glycol. The mechanism for the dispersion and aggregation of silver nanoparticles in ink is discussed. The strong electrostatic repulsions of the carboxylate anions of the adsorbed polyacrylic acid molecules disturbed the aggregation of metal particles in solutions with a high pH value (pH > 5). An inkjet printer was used to deposit this silver nanoparticle-based ink to form silver patterns on photo paper. The actual printing qualities of the silver tracks were then analyzed by variation of printing passes, sintering temperature and time. The results showed that sintering temperature and time are associated strongly with the conductivity of the inkjet-printed conductive patterns. The conductivity of printed patterns sintered at 150 °C increased to 2.1×10^7 S m^{-1}, which was approximately one third that of bulk silver. In addition, silver tracks on paper substrate also showed better electrical performance after folding. This study demonstrated that the resulting ink-jet printed patterns can be used as conductive tracks in flexible electronic devices.

1. Introduction

In the last few years, there has been growing interest in inkjet printing for use in various applications [1–4]. The advantages of inkjet printing include the ease with which it can be used to form high-speed pattern, its low cost, and its applicability to various substrates [5–8]. Inkjet printing is particularly attractive technology to manufacture devices on flexible substrates [9,10]. In all flexible substrates, paper is by far the cheapest and most widely used in daily life, and paper has gained attention because of it is recyclable, lightweight, and biodegradable [11,12], leaving a negligible environmental footprint [13]. Inkjet printing is particularly attractive for realizing direct metallization on paper substrate in fabrication of electronic circuits or devices because most of

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electronic devices require contacts and conductive structures, and metals are the primary choices due to their high conductivity [14]. Applications include radio frequency identification tags (RFIDs) [15,16], sensors [17], electronic circuits [18], RF energy harvesting and wireless power transmission devices [19].

To successfully produce metal tracks and patterns on paper substrates by inkjet printing, stable metal inks with high quality were needed to be produced. Metals inks based on metal nanoparticles and organometallic precursors are two choices [20,21]. Metal nanoparticle-based inks are advantageous for use on paper due to the limited penetration of metal particles into this porous substrate. The metals that have been developed for use in nanoparticle-based inks include gold (Au) [22–24], silver (Ag) [25], and copper (Cu) [26–28]. Because bulk silver has the lowest resistivity (1.6 μΩ cm), and because copper nanoparticles oxidize spontaneously in air [29] and gold is expensive, silver has been most widely used and reported.

Different capping agents are used to tailor silver nanoparticle properties. Short chain carboxylic acids (C_6–C_{10}) [30], poly(vinyl pyrrolidone) (PVP) [31,32], and polyacrylic acid (PAA) [33] have been used as surface-capping molecules to control the particle size. It is important to study the mechanism for the dispersion and aggregation of silver nanoparticles to improve the stability of silver ink. Additionally, it is necessary to sinter printed patterns to remove the organic residues and produce highly conductive structures. The sintering temperature may affect the properties of flexible substrates, especially paper. However, silver nanoparticles can exhibit good conductivity when sintered at approximately 200 °C–350 °C [34,35], which is incompatible with many plastic and paper substrates used in flexible electronics. In order to shorten sintering time and lower sintering temperature, several sintering methods, which can be performed even at room temperature, were recently developed based on coalescence of metal NPs triggered by chemical agents [36], such as NaCl [37] and HCl vapor [38].

In this study, we report the preparation of inks containing well-dispersed polyelectrolyte-capped silver nanoparticles. Additionally, we studied the mechanism for the dispersion and aggregation of the silver nanoparticle-based ink. We also investigated the influence of printing passes, sintering temperature and time on the electrical resistivity and morphology of inkjet-printed patterns. The application of stable silver nanoparticle-based ink in conductive patterns was also presented.

2. Experimental section

2.1. Materials

All of the chemical reagents used in these experiments were purchased from commercial sources with analytical purity and used without further purification. Silver nitrate ($AgNO_3$), triethanolamine (TEA), ethanol, ethylene glycol (EG), and nitric acid (HNO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyacrylic acid (PAA, MW ~3000) and 2-amino-2-methyl-1-propanol (AMP) were purchased from Aladdin Industrial Inc. Deionized water was used in all of these experiments. Kodak premium photo paper ("photo paper" for short) was used as the paper substrate. This photo paper consists of 9 layers and the root-mean-square (RMS) roughness of the photo paper is 18 nm [39] (More detailed description of the photo paper, see Supporting information).

2.2. Preparation of silver nanoparticles and inks

In a typical synthesis, 10 g $AgNO_3$ was dissolved in 10 g deionized water in a beaker with stirring to form a colorless and transparent solution. Then, a mixture (pH ~ 9) of 0.25 g PAA, 30 g TEA and 20 g deionized water was added dropwise to $AgNO_3$ solution with continuous magnetic stirring. The reaction mixture was stirred for 24 h. Next, the products were precipitated by adding ethanol. To remove the unreacted organic and metal salts, the mixture was filtered and washed with copious amounts of ethanol. Finally, the silver nanoparticles were dried at 60 °C. The solid form of silver nanoparticles can be stored and transported conveniently.

Silver nanoparticle-based ink with a solids loading of 20 wt% was prepared by adding a mixture of ethylene glycol and water (3:7 by weight) to the silver nanoparticles. The viscosity and surface tension of this as-prepared silver nanoparticle-based ink were 5.46 mPa s and 41 mN m^{-1}, respectively.

2.3. Fabrication and treatment of silver patterns

Silver patterns were deposited on photo paper by inkjet printing technology, which was similar to the technique used in our previous work [40]. Inkjet printing was performed with a common color printer (Epson Stylus Photo R230), whose print head has 6 rows of orifices, with each row feature 90 orifices measuring approximately 28 μm in diameter. Although the printer has six ink containers, we use only one the container intended for black ink for our silver ink in this study. The silver nanoparticle-based ink was ultrasonically for 10 min, filtered through 0.22 μm membrane and loaded into the cartridges. The ink was printed onto paper, and the bead was air-dried for 5 min between printings. The inkjet-printed silver patterns were sintered at various temperatures between 25 °C and 150 °C for 10 min in air.

2.4. Characterization

Structural characterization of silver nanoparticles was carried out using X-ray diffraction (XRD) with a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ = 0.1542 nm). The morphology and size of as-synthesized silver nanoparticles were characterized by transmission electron microscopy (TEM, Tecnai, F20, 200 KV). The texture of silver tracks was measured with Leica DM 2500 optical microscopy (OM). Particle sizes were evaluated by dynamic light scattering (DLS), and zeta-potential analyses were performed using a Zetasizer nano-SZ (Malvern Instruments). The surface morphology and thickness of the silver lines were observed with a Hitachi S-4800 field emission scanning electron microscope (FESEM) using an operating voltage of 8 kV. The electrical resistivity of the silver patterns was detected by a 4-point probe system (Lucas-Signatone Pro4-4000) and calculated using the geometric dimensions of the patterns.

3. Results and discussion

3.1. Properties of silver nanoparticles

Fig. 1 presents the scheme for the synthesis of silver nanoparticles from silver nitrate. TEA and PAA were used as reducing agent and capping agent, respectively. After adding TEA and PAA to silver nitrate solution, the mixture undergoes a gradual change from colorless to dark black, which coincides with the nucleation and growth of silver nanoparticles. When TEA and PAA were added gradually to $AgNO_3$ solution, the reduction of Ag^+ proceeded slowly, and then the concentration of Ag^0 approached the critical concentration for nucleation. When nucleation occurs, some Ag^0 species convert to nuclei, some Ag^+ are reduced continuously to Ag^0, and the nucleation step continues for a relatively long period of time. As the silver nanoparticles grow, the mixture gradually becomes dark and turbid because large particles reflect and scatter