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Amphiphilic silver particles for conductive inks with controlled wetting behavior

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HIGHLIGHTS

- Synthesis of amphiphilic silver particles.
- Surface modification of silver particles by amidation.
- Dispersion, contact angle, surface tension of silver inks.
- Aerosol jet printing of silver inks on polyimide.
- Conductivity by thermal and photonical annealing.

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ABSTRACT

Silver inks find applications in printed electronics as conductive electrodes. Amphiphilic silver microparticles are prepared by modifying PAA-capped particles with functional amines via an amidation reaction. These modified silver particles can be dispersed in a wide variety of solvents ranging from water ($\varepsilon = 80.4$) to lipophilic alcohols ($\varepsilon = 3–17$) to yield conductive inks with tunable wettability. Using these inks, we have demonstrated aerosol jet printing of conductive silver patterns (36 μm wide, 1.2 μm thick) on Kapton. Electrical resistivity of 3.7 μΩ cm is obtained after thermal annealing at 225 °C for 5 min. Similar electrical resistivity (3.9 μΩ cm) is achieved after photonic annealing as short as 1 ms at 1.4 KV.

1. Introduction

Conductive metallic inks are widely used in printed electronics, such as photovoltaics [1,2], displays [3,4], batteries [5,6], sensors [7,8], and biomedical devices [9,10]. Currently, silver is the most widely used conductive material for these applications representing over 90% of the materials used in a $1.5B annual market. Hence, the ability to control the dispersion of silver particles and concomitantly formulate conductive inks with controlled surface tension, contact angle, and viscosity are critically important. Here, we demonstrate a facile route for synthesizing amphiphilic silver microparticles that can be readily dispersed in a wide range of solvents yielding inks with controlled wetting behavior.

Metal particles are typically synthesized in solution via reduction of metal precursors in the presence of surface capping agents and reducing agents [11–13]. Depending on the capping agent chemistry, the resulting particles are usually either hydrophilic [14,15] or lipophilic [16–18]. Recently, amphiphilic silver particles have been produced by using amphiphilic polymers [19–25] as capping agents during synthesis or by ligand exchange [18,20] after particle synthesis is completed. However, each of these approaches has inherent limitations. For example, amphiphilic polymer capping agents typically form micelles in solution that serve as tiny reactors limiting the overall particle size. Ligand exchange allows better control over particle size, but it is difficult to ensure stability of particles with tunable wettability.

Here, we report a facile synthesis route for creating amphiphilic silver microparticles using a simple amidation reaction [26–28]. We first create silver microparticles using water-soluble poly(acrylic acid) (PAA) as a capping agent. Next, we modify their surfaces by amidation reaction through a carboxy-amine coupling reaction

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(Fig. 1). This two-step synthetic procedure allows us to produce silver particles in water and then control their surface chemistries by the choice of the appropriate amine chemistries. There are three classes of amines of interest, (1) alkyl-terminated, (2) alcohol-terminated, and (3) hybrid-terminated amines (Table S1). We chose 3-morpholonopropylamine (MPA), which possesses an amine (NH_2) group, a propyl ($-CH_2-CH_2-CH_2-$) group, and a morpholino ($-NC_4H_8O$) terminal group, such that its hydrophilic–lipophilic balance (HLB) after amidation can become 7 (Table S2).

2. Experimental

Amphiphilic silver microparticles are synthesized by a modified process of our previous report [29,30], followed by surface modification by amidation reaction. In a typical procedure 8.4 g PAA (molecular weight = 5000 g mol^{-1}, 50 wt% aqueous solution) and 4.2 g PAA (molecular weight = 50,000 g mol^{-1}, 25 wt% aqueous solution) are dissolved in a mixed solution of 500 g water and 280 g diethanolamine (DEA) by stirring for 1 h at room temperature. While stirring vigorously, 140 g silver nitrate powder is added into this solution, followed by stirring for 30 min at room temperature. The resulting solution is then stirred at 80 °C for 2 h. This step results in a mean particle size of 150 nm in diameter (Fig. 2). After cooling for 2 h, acetone (1200 ml), a poor solvent for the PAA capping agent, is added in order to induce particle precipitation. After decanting the supernatant, the coagulated particles are centrifuged at 5000 rpm for 30 min to further concentrate the particles. The concentrated particles are re-dispersed in 100 ml of water, sonicated for 1 h at room temperature, and precipitated again by adding 500 ml acetone. After decanting the supernatant, the precipitates are collected by centrifuging at 5000 rpm for 30 min (Fig. 1).

Surface modification of the PAA-capped silver microparticles is carried out by amidation reaction using functional amines. In a typical procedure, 25.4 g of the washed silver precipitates (89.1 wt% solids as silver, PAA/Ag = 0.012 by wt.) are dispersed in 50 ml *N*-methylpyrrolidone (NMP) by sonicating for 3 h in water bath in the presence of 2.25 ml 3-morpholinopropylamine (MPA) and 2.38 ml *N*,*N*′-diisopropylcarbodiimide (DCI) as reaction activation agent (Fig. 1). The dispersion is then sonicated in a heated water bath at 65 °C for 12 h, followed by particle collection by centrifugation at 9000 rpm for 6 h. The particles are re-dispersed in different solvents by sonicating for 30 min in a water bath at room temperature.

Aerosol jet printing is carried out on a polyimide (Kapton, CS Hyde Co.) and cover glass (VWR Cat. No. 48366-089) substrates using a printhead (Optomec) attached onto a 3-axis micropositioning stage (ABG 10000 x–y–z motion stage, Aerotech Inc.), whose motion is controlled by computer-aided design software. A silver ink (27.5 wt% solids, 1:1 water:IPA by volume, 2.5 cP at 10 s^{-1}) is loaded in a glass vial and aerosols are formed using an ultrasonic atomizer at 45 V. The formed aerosols are translated onto substrates by a deposition nozzle (ϕ = 150 μm, Optomec) using a N_2-powered pressure controller. The sheath and core gas flow rates in the deposition nozzle depend upon ink rheology, nozzle diameter, and printing speed, but typically range from 10 to 100 sccm at 1–10 mm s^{-1}. Printing is performed under ambient conditions at a relative humidity of 40–50%.

Contact angle and surface tension of silver inks are measured by a goniometer (DSA100, Kruss). The silver particles and printed features are observed using a field emission scanning electron microscope (FESEM, Ultra55, Zeiss) after sputtering with Au/Pd for 30 s (EMS 300T D Sputter Coater). Printed silver features are annealed by a hotplate (HS40A, Torrey Pines Scientific) and photonic annealing system (Sinteron 2000, Xenon Corp.). Their electrical resistivity is measured using a four-point probe (RM3000, Jandel).

3. Results and discussion

Fig. 2 shows SEM images and size distributions of the silver microparticles before and after surface modification. Silver particles with mean particle size of 150 nm are obtained (Fig. 2a and b).

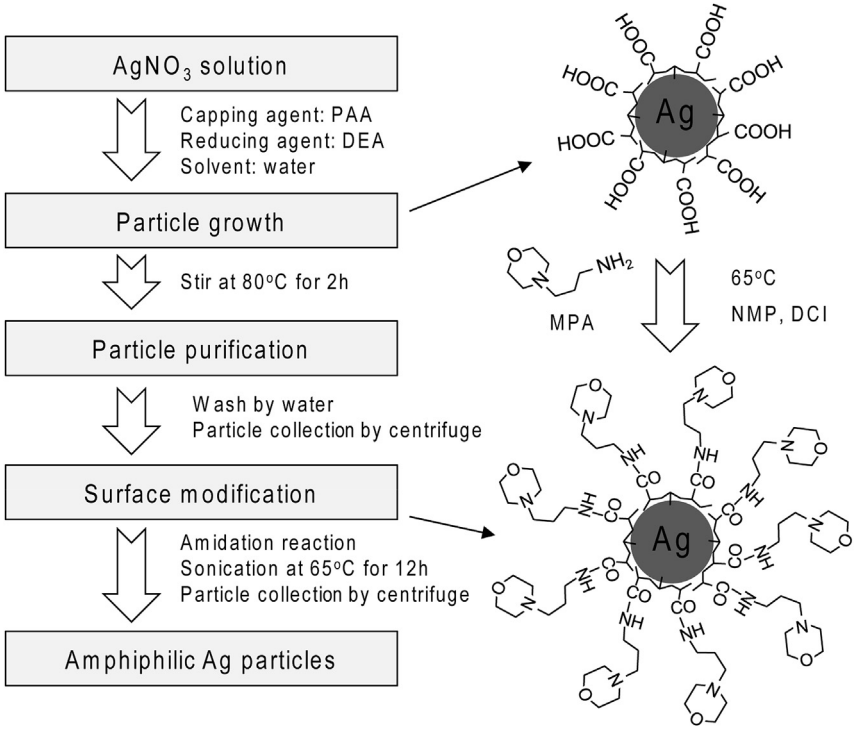

Fig. 1. Flow diagram and schematic illustration of PAA-capped Ag microparticle synthesis and surface modification by amidation reaction using MPA.