

Room temperature sintering of printer silver nanoparticle conductive ink

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Abstract. Future electronics devices are not only smaller and thinner, but are also flexible, bendable and even wearable. This evolution in technology requires direct printing of patterns onto any substrate using conductive inks made of a dispersion of metallic nanoparticles. In this study, Cl⁻ ions was used to induce spontaneous sintering of silver nanoparticles (Ag NPs). Ag NPs with an average diameter of 56 nm were synthesized by polyol method using silver nitrate (AgNO₃) and ethylene glycol (EG) as precursor and solvent, respectively. Poly(vinyl pyrrolidone) was used as the capping agent. Water-based inks were formulated containing different Ag NP loading (10–25 wt %). Using 50 mM NaCl aqueous solution as the dispersing medium, an ink with 15 wt % Ag exhibited a sheet resistance of about 2.85 Ω/sq. This very low sheet resistance was attributed to sintering of Ag NPs, which was accompanied by an increase in average diameter of nanoparticles from 56 to 569 nm.

1. Introduction

Conventional patterning of conductive line on a substrate is done through complex traditional steps, which may include electroplating, vacuum deposition, etching and photolithography. These processes are laborious, expensive, and energy intensive. Large quantities of waste are also produced due to corrosive chemical agents and inefficient materials usage [1-2]. Presently, researches are focused on conductive inks that can be printed directly onto thinner and more flexible substrates, i.e. polymer substrates, to create more complex circuit patterns [3-4].

Conductive inks are usually made of a dispersion of metal nanoparticles and a carrier solvent [3-4]. The small diameter of the nanoparticles minimizes nozzle clogging in print heads of industrial printers. However, the small particle size of nanoparticles induces agglomeration to reduce the surface energy [4-5]. Thus, stabilizing agents are added to prevent agglomeration and generally improve the dispersability of nanoparticles [4-8]. Examples of stabilizing agents include polyacrylic acid (PAA) [8-10], diethylamine [11] and gelatin [4-8].

Metal nanoparticle inks are typically composed of copper (Cu), gold (Au) and Ag nanoparticles. Among these metals, Cu is the most economical. However, it easily oxidizes, which significantly decreases its conductivity [1-2, 4-8]. Au nanoparticles exhibit high conductivity and thermal stability. But Au is too expensive for mass production [12]. Conductive patterns made by printing of metallic nanoparticles generally requires a post-treatment process, i.e sintering at high temperatures, to achieve the required conductivity. This is done to induce coalescence among the nanoparticles and ensure physical continuity for electron flow [11-12]. However, such harsh process complicates printing on heat-sensitive substrates, such as paper and plastics [3-4, 8-9].



There are different methods to achieve low temperature sintering, including low-pressure plasma [13], microwaves [14], laser [15], and use of chemical agents [3, 9, 16]. For example, patterns made of Ag NPs capped with PAA can undergo a built-in sintering mechanism due to exposure to NaCl [9]. Similar approach was used to induce sintering of Ag NPs capped with PVP [16]. In this study, sintering of Ag nanoparticle ink prepared with PVP was achieved at room temperature using NaCl as sintering agent. The effects of Ag loading on the physical continuity and electrical resistance of the pattern produced were also investigated.

2. Methodology

The Ag NPs were prepared by first dissolving 0.1 g AgNO₃ and 0.4 g PVP (MW = 10,000) in 20 ml ethylene glycol, then heating at 160 °C for 14 min under reflux and constant stirring. The precipitates were then collected by centrifugation and washed several times with ethanol. The Ag nanoparticles were observed under scanning electron microscopy and analyzed by X-ray diffraction.

3. Results and discussion

Figure 1 shows an SEM image of Ag NPs synthesized at 160°C using polyol method with and without the sintering agent, NaCl. The Ag NPs have an average diameter of 56 ± 6 nm. The uniform size distribution is attributed to the similar growth rate of the Ag nanocrystals during synthesis, as well as to the steric hindrance provided by PVP. Then again, the presence of PVP layer around the nanoparticles prevents interconnection and typically results in high resistivity in printed conductive ink. The corresponding XRD pattern in Fig. 2 shows only peaks attributed to metallic Ag. Five distinct diffraction peaks at $2\theta = 38.2, 44.4, 64.5, 77.5$ and 81.6° were indexed to the (111), (200), (220), (311) and (222) reflections of metallic Ag (JCDPS File No. 04-0783). The sharp XRD peaks indicate the high crystalline structure of the as-prepared Ag NPs. No other peaks attributed to AgNO₃ or other compounds were identified, which suggests high purity of the Ag product.

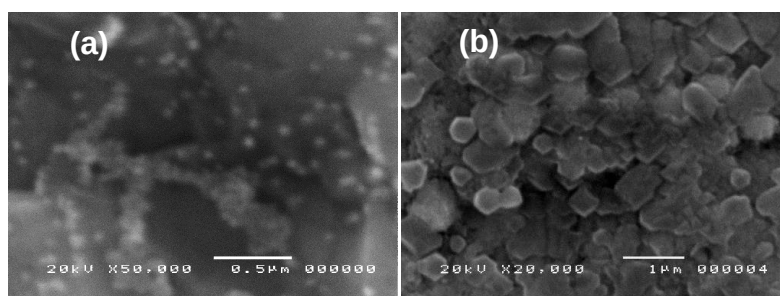


Fig. 1. SEM images of as-prepared Ag NPs (a) without and (b) with 50mM NaCl in the dispersing medium.

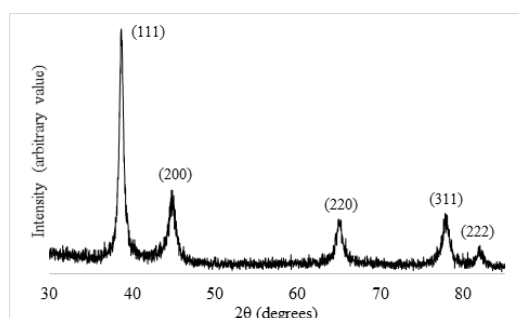


Fig. 2. Corresponding XRD pattern of as-prepared Ag nanoparticles.

On the other hand, an obvious increase in the particle size was observed after dispersion of Ag NPs in 50 mM NaCl aqueous solution. Large Ag particles with a mean diameter of about 569 nm were obtained as seen in Fig. 1b. This is approximately 916 % larger than the diameter of the as-prepared Ag NPs in Fig. 1a. It has been reported that Cl^- ions can cause the detachment of capping agents, such as PVP that surround the nanoparticles [3,9,16]. Due to high affinity of Ag with Cl^- ions, PVP molecules are possibly desorbed from the surface of the nanoparticles. The detachment of PVP probably causes destabilization, which increases the surface energy of the NPs. [3,9,16]. The atomic mobility caused by the increase in surface energy of the nanoparticles promotes agglomeration and their eventual sintering to further reduce the surface energy as shown in Fig. 3. The resistivity of 20 μL Ag NPs dispersed in 50 mM NaCl aqueous solution after deposition onto a glass substrate was measured to be about $2.85 \Omega/\text{sq}$. Without NaCl, no sheet resistance value was measured for the Ag nanoparticle ink at the same nanoparticle loading.

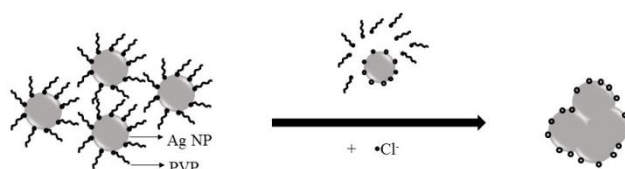


Fig. 3. Sintering mechanism for Ag NPs capped with PVP using Cl^- ions as sintering agent.

Instead of adding NaCl into the Ag NP ink, the effect of soaking in saturated NaCl solution of the Ag NPs pattern on glass substrate was also studied. Figure 4 shows the SEM image of a droplet of 20 wt % Ag NP in deionized water before and after soaking in saturated NaCl solution for 30 min. Similarly, the average diameter of the Ag NPs was increased to 303 nm, which is 441% larger than the diameter of the as-synthesized nanoparticles in Fig. 4a. The nanoparticles also have a wide size distribution, which could be attributed to Ostwald ripening [3,9,16]. The presence of large particles suggests that sintering and growth possibly occurred.

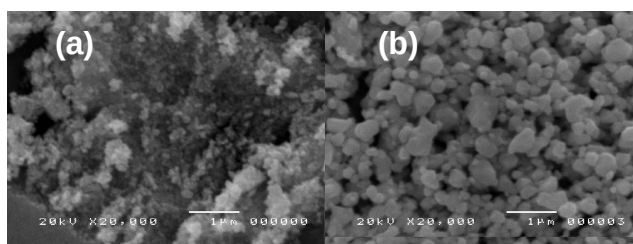


Fig. 4. SEM images of 20 wt % Ag NP in DI water (a) before and (b) after soaking in saturated NaCl solution for 30 min.

Figure 5 shows the change in sheet resistance with increasing AgNP loading in a water-based ink. Patterns were deposited on glass, followed by immersion in a saturated NaCl aqueous solution for 30 min. As seen in Fig. 5, there is a large difference between the sheet resistances of the ink containing 10 and 15 wt % Ag loading. At higher AgNP loading, more nanoparticles come into contact upon detachment of the PVP. The lowest sheet resistance of $97.33 \text{ m}\Omega/\text{sq}$ was obtained from the ink sample with 25 wt % Ag. In order to test the applicability of the developed Ag NP ink in paper electronics, the patterns were used to complete a circuit containing a power source and light-emitting diodes (LED). Essentially, all the patterns were able to light up the LED assembled in a circuit without any annealing as shown in Fig. 6. The paper also underwent bending and folding as shown in Fig. 6c.

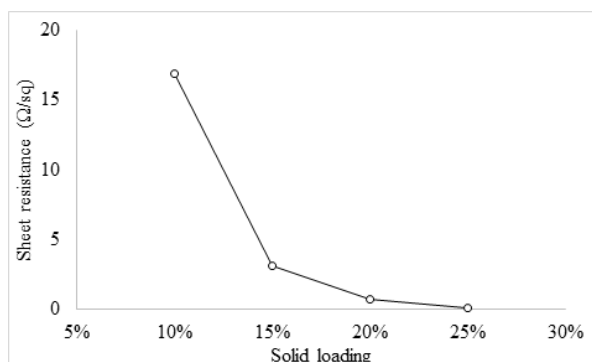


Fig. 5. A plot of sheet resistance (Ω/sq) with increasing Ag NP solid loading (wt %) for a water-based ink. Patterns were deposited on glass substrate then soaked in a saturated NaCl solution for 30 min.

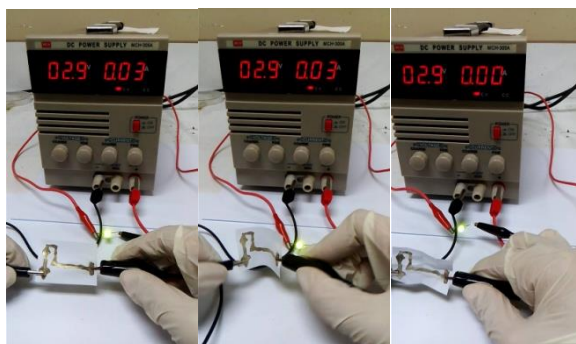


Fig. 6. A pattern made on a bond paper using the formulation containing 15 wt % Ag NP in 50mM NaCl solution being able to light up an LED (a) even after bending (b) and folding (c), the inset shows the bond paper bent in half four times.

4. Conclusion

Uniformly distributed Ag NPs with an average diameter of 56 nm were synthesized through a polyol method. PVP was employed as the capping agent. After dispersing the Ag NPs in 50 mM NaCl, the average diameter of the nanoparticles increased to 569 nm. The pattern achieved a sheet resistance of about $2.85 \Omega/\text{sq}$. Without NaCl, the pattern was not conductive. This indicates that Cl^- ions removed PVP on the surface of the nanoparticles, leading to their agglomeration and eventual sintering. The effect of Cl^- ions as a sintering agent was further explored by soaking the patterns made with increasing Ag loading in saturated NaCl solution. After 30 min soaking, the diameters of the nanoparticles increased, promoting true continuity in the pattern. As a result, the sheet resistance was decreased.

5. References

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