Original Article

One-step synthesis of Ag nanoparticles for fabricating highly conductive patterns using infrared sintering

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\textbf{ABSTRACT}

Synthesizing metal nanoparticles (NPs) for conductive nano-ink applications on a large-scale and in a green, facile method is important. Here we use an ultrasonic-assisted method to synthesize Ag NPs with an average diameter of 15.5 ± 1.0 nm in poly(N-vinylpyrrolidone) (PVP) solutions containing ascorbic acid (Vc) and glucose as mixed reducing agents. TEM, HR-TEM and XRD analysis confirmed the purity of Ag NPs. A thin, mixed Vc and PVP layer on the surface of the Ag NPs, confirmed by TGA and FT-IR, offered the air-stability of the Ag NPs. A rapid and effective sintering method was employed to obtain highly conductive patterns and avoid substrate damage. Upon sintering, the mixed layer quickly decomposed to obtain a highly conductive net. Infrared sintering at 15 W for <60 s was used to make conductive patterns whose resistivity reached up to 7.4 ± 0.5 μΩ cm, 4.6 times that of the bulk Ag. Three methods of the pattern designs were tested for conductivity and applicability. A sample paper-based electrode, RFID antenna, and our school logo were successfully printed and all exhibited good flexibility and conductivity. Both the synthesis and sintering process can be easily integrated into one machine, which is promising for future applications.

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1. Introduction

Flexible printed electronics are frequently used in various applications such as displays [1], transistors [2], antennas [3], sensors and batteries [4,5], and are attracting researchers to perform innovating work in this field. Compared with traditional rigid microelectronics, flexible electronics have advantages making them wearable, stretchable, and easy to design quickly [6]. Further, the process of preparing conductive patterns on a flexible substrate is critical for manufacturing.

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Photolithography technology, sputter coating, and airbrushing are used to produce conductive patterns on flexible electronics. However, these methods are complicated and costly, and waste is unavoidable. Inkjet printing and similar methods are low cost and fast with minimal waste being produced, which is advantageous for printing electronics in large industrial production environments.

Good quality conductive inks are critical for forming conductive patterns after sintering. Carbon, conductive polymers, and metal-organic complexes are commonly used as the conductive materials. Metal-based inks composed of metal nanoparticles (NPs) possess high conductivity. However, the high cost of Au and easy oxidation of Cu limit their application [7,8]. Most studies have focused on novel Ag NPs [9,10]. However, most of the research involves complicated processes with high temperatures, and there are few studies using one-step process at room temperature. The reported one-step syntheses of metal NPs were usually at higher temperatures over 100 °C–150 °C [11,12], and those at room temperature were typically involving rare-earth metals [13], such as Ga and In, which were costly and caused pollution. Thus, a simple method for producing Ag NPs at room temperature with large production capacity and environment-friendly is needed.

The main challenge in obtaining highly conductive patterns is that the metal NPs need to possess anti-oxidation stability. Typically, capped molecules such as poly(N-vinylpyrrolidone) (PVP), polyvinyl alcohol (PVA), sodium dodecylbenzenesulfonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) are applied on the NPs surface [14–16]. In order to remove the capped molecules, heating to a temperature higher than 200 °C and holding for >30 min is required [17]. The high-temperature limits possible substrates and the long processing time increases the cost and the oxidation of the metal particle. Efficient sintering methods were also developed, such as laser beam, a low-pressure argon plasma, microwave & photonic radiation [18–20]. Perelaer et al. developed roll-to-roll compatible sintering with <15 s [21], which can greatly reduce sintering time and cost.

In this study, a facile approach was explored to synthesize Ag nanoparticles and its flexible conductive patterns. Air stable Ag NPs were synthesized under ultrasonic processing at room temperature using PVP as the capping agent and ascorbic acid (Vc) as both the capping and reducing agent. Nano-inks composed of Ag NPs were prepared and patterns were produced by three printing methods. Poly-dimethyl sulfoxide (PDMS) and paper photo substrates supported flexibility and foldability of the conductive pattern were produced via infrared sintering under the air atmosphere. The integration of the ink-jet processing and infrared sintering into one machine was demonstrated to be more environment-friendly and reduce the possibility of undesirable reactions occurring between the two processes, such as oxidation.

2. Experiment

2.1. Materials

Poly(N-vinylpyrrolidone) (PVP) (Mw = 40000, >99%) and cetyltrimethyl ammonium bromide (CTAB, 99%) were supplied by Alading Co. Ltd, Shanghai, China and used as capping agents. Ascorbic acid (Vc, 99%) and glucose (C6H12O6) were purchased from National Medicines Co. Ltd, Shanghai, China and used as mixed reducing agents. Silver nitrate (AgNO3, 99%), sodium hydroxide (NaOH), ethanol, diethylene glycol (DEG, >99%), ethylene glycol (EG, >99%) and glycerol (99%), supplied by Chemical Reagent Company, Tianjin, China, were used for preparing Ag NPs and Ag nano-ink. All agents were of analytical purity.

2.2. Synthesis of Ag NPs

For a typical preparation in ambient atmosphere, 0.5 g, 1.0 g, and 1.5 g of Vc were respectively mixed with 0.3 g of glucose in a single-neck round-bottom flask containing 30 mL distilled water, followed by magnetic stirring for 30 min. This was Solution A. 0.5 g AgNO3 and 0.25 g, 0.5 g, PVP were respectively dissolved in 10 mL distilled water with magnetic stirring, and 0.23 g of NaOH was added quickly to adjust the pH to 10. This was Solution B. Solution A was added quickly to Solution B under ultrasonication. The color of the solution changed nearly instantly from transparent to dark. After 30 min at room temperature, the resulting particles were separated by centrifugation and washed with distilled water and ethanol. Pure Ag NPs were obtained and dried in air for further studies.

2.3. Preparation of Ag ink and its corresponding patterns

To acquire high-quality nano-Ag ink, the Ag NPs were redissolved into mixed solvents with different evaporation rates of water, ethanol, glycerol, and ethylene glycol at corresponding volume fraction ratios of 23:8:30:5:38.5 to form a surface tension gradient between the solvents. Nano-ink containing 20–60 wt% Ag NPs was obtained and used for printing or drawing flexible printed patterns. Figs. 1a and b schematically show the procedure of the Ag nano-ink process.

Complicated patterns prepared from the Ag nano-ink were created on photo paper using an office printer (HP Deskjet 1010). Fig. 1c shows the printing and sintering of Ag patterns with an infrared-heated lamp for 0–60 s with power of 5–20 W. All printing and sintering experiments were performed at room temperature with an air atmosphere.

2.4. Characterization

X-ray powder diffraction (XRD) patterns of the nano-particles were obtained and analyzed using a JEOI D/Max2500pc diffractometer with CuKα radiation (λ = 1.54059 Å). The size and morphology of the Ag NPs were characterized by transmission electron microscopy (TEM) on a JEOI JEM-2100 instrument at 200 kV. Ag colloids were monitored by TU-1901 UV–vis spectrometer using a quartz cell in the range of 300–700 nm. Dried Ag NPs were ground with KBr and compressed into a circle flake (13 mm diameter) for FT–IR analysis. Thermogravimetric analysis of the Ag NPs was performed with a NETZSCH STA 499C. The particles were heated to 800 °C at a ramping temperature of 10 °C min−1 in Ar atmosphere. Ag pattern microstructures were examined using a Hitachi S-4800 SEM. Printed pattern resistances were measured using a digital mul-
3. Results and discussion
3.1. Characteristics of Ag NPs

A capped polymer layer on the NP surface can prevent metal oxidation. In this study, PVP and Vc were used as the mixed capped polymers, and Vc and glucose were used as the reducing agents. TEM and HR-TEM images, and XRD patterns of Ag NPs are shown in Fig. 2. The average diameter of the Ag NPs was approx. 15.5 nm (Fig. 2a), which was consistent with the dark brown color of the metal conductive ink, shown in the inset picture. The lattice fringes of Ag is shown in Fig. 2b, with a spacing of approx. 0.24 nm and 0.14 nm, corresponding to the (111) and (220) lattice spacing planes of Ag, respectively. XRD patterns shown in Fig. 2c contain four main peaks at $2\theta = 38.2^\circ, 44.4^\circ, 64.6^\circ$ and $77.5^\circ$ corresponding to (111), (200), (220) and (311) planes, respectively, of face-centered cubic (fcc) Ag. Impure phase peaks were not observed in all the patterns, indicating the obtained Ag particles possessed excellent anti-oxidation property.

To observe the function of the silver nanoparticle with the reducing and capping agents, XRD patterns of the Ag NPs with different masses of Vc, PVP, and CTAB obtained, as shown in Fig. 3. The FWHM of the four characteristic peaks increased with increasing of Vc and PVP from 0.5 to 1.5 and 0 to 0.5, respectively (Sample 1–3, Table 1). The average size of the particles measured by the Scherrer formula decreased from 34.3 nm to 15.5 nm indicating the combination of Vc and PVP reduced the particle size, as shown in the XRD patterns a to c in the Figure. Decreasing the mass of Vc and adding CTAB
reduced the particle size to 16.9 nm, as shown in the XRD patterns d to e (Sample 4 and 5). These results show that the Vc, PVP, and CTAB mixed capped layer is thin, which will be shown to increase the conductivity of Ag nano-ink printed patterns. In addition, it is well known that the assistance of ultrasonic treatment provides unusual physical and chemical effects [22,23], which supplies the additional and effective energy for particles forming process, and also makes the formation of more particles easily. This makes lots of silver particles form in a few seconds when the Ag⁺ ions meet the reducing agent, and then the coating molecules can be quickly and completely adsorbed on the surface of Ag particles. Thus the obtained particles have good anti-oxidation properties with the thin coating layer. Using the similar method, Cu and Au particles, and their corresponding nano-inks can also be obtained, respectively (Supporting information, Fig. S1).

The pH value of reaction solution was shown to play an important role in metal nanoparticle stability. UV–vis absorption spectroscopy was carried out to further analyze the Ag NPs obtained in pH values ranging from 7.0 to 11.5. As shown in Fig. 4a, the spectrum of Ag NPs showed peaks ranging from 418 to 409 nm, consistent with the surface plasmon resonance absorption band of silver nanoparticles at 400–420 nm [24]. At a pH value close to 10, the peak is approx. 409 nm, indicating that the diameter of the nanoparticles was reduced, consistent with the TEM analysis in Fig. 2a. Fig. 4b shows the appearance of obtained nano-ink in the bottles. The sample color changed gradually from light brown to dark and back to light brown, indicating that the diameter of the nanoparticles initially decreased and then increased, consistent with the measurement by Scherrer formula. This result confirms that changing pH value is an effective in controlling the activity of PVP and Vc, leading to air-stable Ag NPs with a reduced size.

3.2. Thermal stability and FT-IR spectroscopy of Ag NPs

The capped polymer layer on the Ag NP surface not only avoids silver oxidation but also prevents particles from dense packing in the subsequent sintering process, resulting in an increased resistance. Thus, pure Ag NPs capped with a thin capped polymer layer have the advantage of decreasing the resistance of the corresponding conductive patterns. Fig. 5a shows the thermal decomposition curves of the Ag NPs with different mass ratios of Vc, PVP, and CTAB capped Ag NPs. The corresponding thermal decomposition of Vc, PVP, and CTAB started at 190 °C, 380 °C and 220 °C, respectively. As shown in Fig. 5b, weight loss occurred from 25 °C to 190 °C, which is attributed to the loss of residual alcohol and physisorbed water in the material. When the temperature increased to >190 °C, weight loss drastically increased. This is attributed to the gradually decomposing of the organic capping layer, most notable with Vc/CTAB-capped Ag NPs and Vc/CTAB/PVP-capped Ag NPs. No obvious curve change was observed with Vc-capped Ag NPs. Although the curves of Vc-capped and Vc/PVP-capped Ag NPs are similar, the maximum weight loss of the former was 1.35% higher than that of the later. The use of thermally stable Ag NPs avoids rapid initial oxidation and allows high conductivity patterns to be produced at lower temperatures.

As shown in Fig. 5, it can be found that the mass loss increased with the Vc, PVP and CTAB mixed capping agents and reached up to 10%, indicating a thicker capped layer. The mass loss of the particles capped with Vc/PVP and Vc/CTAB was less than that of Vc/PVP/CTAB-capped Ag silver particles, reaching up to 4% and 1%, respectively. This indicates that the combination of Vc and PVP resulted in the formation of a thinner capped layer, leading to a fast decomposition upon sintering.

FT-IR spectroscopy was used to further investigate the coordinative interactions between Ag NPs and PVP, as well as Vc. Compared with the spectra of pure PVP and Vc, as shown in Fig. 6, the C=O peaks of PVP and Vc at 1660 cm⁻¹ shifted to 1650 cm⁻¹ when Vc was the sole coating agents and to 1618 cm⁻¹ with Vc and PVP co-capping agents, respectively, indicating of that both Vc and PVP were coated on the surface of the Ag NPs. Compared with PVP capped Ag NPs, the frequency of the carbonyl stretch shifted to 1645 cm⁻¹ [25]. This shift is associated with the formation of a coordination bond between silver atom and oxygen atom in the carbonyl group. The band at 1115 cm⁻¹ assigned to –OH of Vc shifted to 1130 cm⁻¹ in the Vc-capped sample, and the intensity greatly.
increased in the Vc and PVP co-capped sample. These results suggest that the molecular Vc was chemisorbed on the particle surface via interaction with C=O and –OH and that PVP molecules was chemisorbed via interaction with C=O and –N–O–H. The cooperation of Vc and PVP makes the coating layers thin and prevents oxidation by forming a completely capped surface on Ag, which is consistent with the analysis of the TGA.

3.3. Flexibility and surface microstructures of Ag pattern obtained by direct writing method

To test the applicability of the Ag nano-ink, Ag patterns were produced using direct writing methods on two different substrates. Fig. 7a and b show the conductive ink writings on a poly-dimethyl sulfoxide (PDMS) substrate. An example of the Ag line/electrode was designed and produced. After sintering,
Fig. 6 – FT-IR spectroscopy of pure PVP and Vc (a) and Ag NPs coated with Vc and PVP/Vc, respectively (b).

the design was bendable in arbitrary directions (Supplement information video 1) and the corresponding resistance was 1.1 Ω (Fig. 7c).

Fig. 7d-f show the conductive ink obtained by directly writing on photo paper substrates. The written silver pattern was shiny before sintering (Fig. 7d and e). After sintering, the pattern can be bent by degree >120° and was not detached from the paper substrates, showing an increased flexibility. After bending over 200 cycles, the resistance was measured to be up to 1.9 Ω (Fig. 8f) and 7.4 ± 0.5 μΩ⋅cm (ρ = Rbh/L, where ρ is the measured resistance, L is the length (6 cm), b is the line thickness (~0.5 cm), and h is the line width (~50 μm). This resistance was 4.6 times greater than the bulk resistance of pure Ag (1.6 μΩ⋅cm). These results show that the conduc-
Fig. 7 – Applications of Ag conductive patterns drawn on PDMS substrate with bending (a, b) and the corresponding resistance measured using a multimeter (c). Flexible photo paper substrate, bending, and corresponding resistance measured by a multimeter (d, e, f).

Fig. 8 – SEM images of Ag written directly on a photo paper as a function of sintering power ranging from 1 W (a), 5 W (b), 10 W (c), and 15 W (d) for 60 s. Corresponding density and area ratio measured by Image J software (e–h).

Table 2 – Comparison of sintering temperature, time, and resistivity (compared with bulk silver) of this work with those found in the literature.

<table>
<thead>
<tr>
<th>Sintering temperature, °C</th>
<th>Sintering time, min</th>
<th>Resistivity, times</th>
<th>Literatures</th>
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<tbody>
<tr>
<td>260</td>
<td>3</td>
<td>10</td>
<td>Ref. [23]</td>
</tr>
<tr>
<td>250</td>
<td>60</td>
<td>10</td>
<td>Ref. [24]</td>
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<td>230</td>
<td>25</td>
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<td>Ref. [25]</td>
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<td>160</td>
<td>120</td>
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<td>Ref. [26]</td>
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<tr>
<td>120</td>
<td>15</td>
<td>9</td>
<td>Ref. [27]</td>
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<td>Room temperature</td>
<td>1</td>
<td>4.6</td>
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The nanoparticle ink has advantages in application for different flexible substrates with a lower resistivity. The nanoparticle ink can absorb the high radiant energy produced by the infrared lamp more readily than a polymer substrate, leading to faster sintering between particles without requiring high temperature, and thus resulting in lower resistivity of the conductive pattern with a flexible substrate. Compared with the traditional thermal sintering at high temperature for a long time [26–30],...
as shown in Table 2, the infrared sintering not only avoids all these problems, but also the obtained patterns possess a relatively lower resistance, and the corresponding flexible electronics/devices can be largely produced in the future.

The microstructure of a conductive pattern is critical to its conductive properties. The microstructure of the silver patterns sintered under various power conditions for 30 s was observed, as shown in Fig. 8. Fig. 8a is for sintering at 1 W power, many small particles exist in their original shape and forming loose pores and weak connections between the particles. As the sintering power increased from 5 to 10 W, the area of pores was gradually reduced and the particles began to deeply connect with each other to form large particles and the connection was strong (Fig. 8b and c). When the sintering power was 15 W, the smaller particles disappeared completely and a more dense, bulk Ag, structure was formed (Fig. 8d). To further analyze the structure after sintering, both the area ratio between the metal and pore structures and the packing density between the particles were calculated using Image J software. As shown in Fig. 8(e–h), corresponding to Fig. 8(a–d), the pore area gradually decreased from 22.77% to 8.82% as the sintering power increased, confirming a more dense structure was produced at higher power of sintering. According to the random packing model proposed by Furnas [31], the fractional packing density of a monosized spherical particle system is 0.65 and a bimodal mixture system is 0.8775 [32]. The particle density increased from 0.7367 to 0.8988, which is higher than the systems mentioned above. This result might be due to: (1) the size distribution of particles is wide and small particles can fit into the pores between the larger ones; (2) more particles deeply connect with each other after sintering and form larger particles or bulk Ag. This result confirms that the patterns become more dense, which is related to sintering power.

3.4. The practicability of Ag pattern obtained by printing methods

Printer-designed conductive Ag patterns were formed using the atmosphere to control the process (Fig. 9a). Complicated patterns can be easily designed including an RFID antenna wherein the bend angle can be designed according to the RFID application (Fig. 9b). At room temperature, Ag patterns show a low resistivity, as shown in Fig. 9c. The sintering power, time, and printing repetitions affect the resistivity of the Ag pattern. As the sintering power and time increased, the resistivity gradually decreased to 15.6 ± 0.8 μΩ·cm at 15 W and 15 s. The increased conductivity of the patterns is the result of easier decomposition of the coating layer on the surface of pure Ag NPs and the external force of the printer increasing the Ag particle density. Fig. 9d and e show the microstructure before and after sintering. The loosely connected nanoparticles are densely packed after sintering.

Office ink-jet printers are widely used in many fields. The logo of our university was designed and produced using such an office ink-jet printer, as shown in Fig. 10. The resolution of the pattern is high and the flexibility is excellent (Supplement Information video 2). The resistivity curve of the printed patterns sintered at 15 W for 15 s for various times is shown in Fig. 10c. Due to being very thin, the resistivity of the film when the pattern initially formed was approx. 1000 μΩ·cm. The resistivity greatly decreased with increasing printing repetitions 3 and 6 times. When printing was repeated for nine times, the lowest and most stable resistivity, 20.6 ± 1.0 μΩ·cm, was achieved, which can be accepted in application. The office printer and the easy sintering method can be used in practical applications. From these analyses, the infrared sintering makes a dense structure in shorter time, which can effec-
tively minimize oxidation and produce a highly conductive pattern.

Comparing the above methods, it can be found that the lowest conductivity was obtained by the direct writing method, which is practical for applications on many kinds of substrates. Lower resistivity and easier design in a portable application were found in the ink-jet printer method. Although the ink-jet printer method has several limitations including multiple printing cycles and a higher resistivity than Ag wire, application substrates can include many kinds of paper. Although ink-jet printing still has limitations such as electrical fatigue and less thermal stability, as a simple, and convenient approach, it is promising to prepare conductive patterns for portable applications requiring fine detail, such as partial conductive materials in 3D printing and so on.

sintering produced a highly conductive net. Infrared sintering was carried out at 15 W for less than 60 s and the quick sintering prevented substrate damage, which is critical for reducing the resistivity of the conductive patterns. A paper-based electrode, RFID antenna, and the logo of our school were designed with Ag nano-ink by direct writing and printer methods. The patterns obtained by the direct-writing had the lowest resistivity, 7.4 ± 0.5 Ω cm, 4.6 times of the bulk resistivity of pure Ag. PDMS and photo paper substrates showed excellent pattern flexibility. The printing methods demonstrated that highly complicated patterns can be produced. All the patterns were of high conductivity and good flexibility. The synthesis of Ag NPs, conductive pattern formation and the sintering methods can be easily combined into one machine, which is promising for future fabrication of printed circuits.

4. Conclusions

In this paper, air-stable Ag NPs 15.5 ± 1.0 nm in diameter were produced by reduction from Ag⁺ ions using ascorbic acid and glucose as mixed reducing agents in PVP solutions in an ultrasonic bath. The reaction was performed at room temperature without protection of inert gas. The obtained particles were confirmed to be pure metallic Ag with an fcc structure by XRD. Adjusting the pH value of the reaction solution to 10, mixed Vc and PVP formed a thin layer on the particle surface, enhancing the air-stability of the Ag NPs, and its fast decomposition upon

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Conflicts of interest

The authors declare no conflicts of interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.10.039.

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