Scalable Synthesis of Monodispersed Branched Submicron Silver Particles as the Printed Electrically Conductive Adhesives Fillers

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Abstract*—Electrically conductive adhesives (ECAs) are an important interconnecting material to electronic packaging industry due to the low processing temperature, fine pitch capability, simple process and mechanical flexibility compared with conventional solder and wiring technologies. Silver micro/nano-particles are widely used as conductive filler owing to their low electrical resistivity, chemical stability and various shapes and morphologies. In this study, we introduce a facile synthetic method of monodispersed branched submicron silver particles which is about 500 nm in size, by reducing the silver salts with $N_2H_4 \cdot H_2O$ in an aqueous solution at room temperature. By tuning the reaction condition, a series of submicron silver particles with acute branches were obtained, and the feature size of each branch is smaller than 20 nm. The highly branched nanoparticles rendered them with a low sintering temperature and a low threshold to enable percolation, which can contribute to a significant increase in electrical conductivity of the ECAs. The ECAs based on these branched submicron silver particles demonstrate low bulk resistivity, which is approximately 1×10^{-4} Ω·cm. On account of the simple, cost-effective, scalable and eco-friendly liquid phase synthetic method, this technology may find potential applications in microsystems packaging and printed electronics.

***Keywords*—electrically conductive adhesive; branched submicron silver particles; printed circuit**

I. INTRODUCTION

Electrically conductive adhesives (ECAs) have received increasing interest as an interconnecting material in electronic packaging industry because of their advantages such as environmental friendliness, simple processes, low processing temperature [1-3] and compatibility to flexible substrates [4]. Typical ECAs are composed of epoxy resin matrix and electrically conductive fillers. The epoxy resin dispersant usually consists of epoxy resin, curing agent, and catalyst, etc. During the curing process, of the shrinkage due to chemical cross-linking, can promote the close contact between silver powder so as to reduce the contact resistance and improve the overall electrical conductivity [5-6]. Compared with other electrically conductive fillers, Silver is the best choice for ECAs owing to its high electrical and thermal conductivity, chemical stability, relatively low cost among noble metal [7-8]. Therefore, the silver-based ECAs are employed as an important electrical and thermal conducting material for electronic packaging, which have been widely applied in thin film transistor (TFT) [9-10], high-power light-emitting diode (LED) attachments, solar cell panels, flat panel display (FPD) panel interconnects, radio frequency identification (RFID) tags, flexible touch panel interconnects, membrane switches, and so on [11-13].

So far, there have been various works on silver-filled ECAs which are aimed to improve the electrical conductivity of the contact parts of silver powder to achieve better spatial percolative efficiency. One way is to adjust the aggregation state of the fillers in the ECAs to form an efficient percolated network by means of mixing fillers of different sizes and shape [2, 4, 14-15]; another way is to modify the filler surface to render a better ohmic contact between adjacent fillers [16-19]. Both of the above mentioned methods often involved nanoparticle to the ECAs, which can increase the viscosity of pastes and percolation threshold in terms of the smaller size and lower degree of anisotropy than the conventional microflake fillers [8, 20-21]. On the other hand, those anisotropic-shaped conductive fillers, such as silver nanowires and microflakes, can significantly decrease percolation threshold [1, 18, 22-23]. But some disadvantages and limitations have emerged for them in the applications of ECAs. For instance, the aggregation problem of nanowires and the impurities introduced from the ball-milling process of silver flakes hinder their performance characteristics as filler materials [1]. Recently, the authors reported that the ECAs based on Ag micro-dendrites with a low-temperature sintering characteristic and an ultra-low electrical percolation threshold of 8 wt% [24-25] can be obtained. It indicated that three-dimensional (3D) nanostructured silver may become a promising alternative when being used as the ECAs.

Herein, we report a facile and efficient method to fabricate monodispersed branched submicron silver particles as ECA fillers for printed electric applications. The preparation process is simple and can take place in aqueous solution at room temperature. It can be scaled up easily. Through adjusting the critical experimental parameters such as molar ratio, concentration and pH value of the reactants, the surface nanostructures and morphology of the branched submicron silver particles can be well controlled. The as-prepared branched submicron silver particles possess unique petal-like nanostructures of about 20 nm in thickness, which achieve highly efficient conductive network and excellent low temperature sintering ability (about 150 °C). Meanwhile, the branched submicron silver particles filled ECAs can be easily printed onto various substrates such as glass and polyethylene terephthalate (PET). All of above advantages mentioned, can

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render the ECAs based on these branched submicron silver particles be more competitive in the emerging printed flexible electronic applications.

II. EXPERIMENTAL

A. Material

Silver nitrate ($AgNO_3$) powder (99%), tween 80 ($C_{24}H_{44}O_6$, 98%), formaldehyde (HCHO) solutions (37 wt% aq.), trisodium citrate dehydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) (99%) and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) solutions (85 wt % aq.) were purchased from the Sinopharm Chemical Reagent Company. The Bisphenol-A type epoxy resin (Epon 828) and methyl nadic anhydride (MNA), were supplied by the Shell Chemical Company and Aladdin Industrial Corporation, respectively. Hexamethylenetetramine (99%) was obtained from Guangzhou Chemical Reagent Factory, China. All chemicals were chemical grade at least and were used as received without further treatment.

B. Synthesis of the Branched Submicron Silver Particles

A standard process for the preparation of branched submicron silver particles is presented in the following. Tween 80 aqueous surfactant solution (0.014 wt‰), formaldehyde solutions (8 mM) and trisodium citrate dehydrate aqueous solution (0.12 M) were mixed together with the volume ratio of 2:1:1 under vigorous magnetic stirring at room temperature. Then, silver nitrate aqueous solution (60 mM) was dropped slowly. After 30 min of reaction, hydrazine hydrate solution (0.12 M) was added. The precipitate was obtained by consecutive washing cycles with deionized (DI) water and ethanol, and then dried in vacuum.

C. Preparation of ECAs and Prototype Formation

For preparing the ECA sample, bisphenol-A type epoxy resin and methyl nadic anhydride (100:85 by quality ratio based on the epoxide equivalent weight of the epoxy resin and the hydroxyl equivalent weight of the hardener) were mixed together, and then mixed with the branched silver particles; together with the reported iodine treatment for surface modification [1, 13]. Hexamethylenetetramine with the concentration of 0.5 wt%, which acted as catalyst, was added to the resin dispersant to accelerate reaction. It was doctor-bladed onto a piece of glass slide, with the gap of 2 mm and the length of 40 mm, which was precisely controlled by two parallel scotch tapes (thickness ~55 μm).

There were two kinds of prototype samples which were the LED arrays and the capacitive touch panel. The conductive trace (30 μm × 2 mm × 70 mm) that connected the LEDs was obtained by doctor-blading the ECAs onto a piece of glass slide, mounting the LEDs on the electrodes. Similarly, the capacitive touch panel was fabricated by screen printing on the PET. All of the ECA samples were precured at 100 °C for 30 min, and then fully cured at 150 °C for 30 min.

D. Characterization and Measurement

The morphology of branched submicron silver particles was characterized by SEM (ZEISS SUPRA® 55, Germany) and TEM (FEI tecnai G2 F30, USA). The crystal property was examined by powder X-ray diffraction at a scan rate of 10 °/min using a Rigaku diffractometer (D/MAX-2500, Japan) equipped with Cu-Ku radiation (λ= 1.5418 Å). The purity of branched silver particles was examined by Fourier transform infrared (Nicolet iS 50, USA) with the wavenumbers from 4,000 to 500 cm^{-1}, and the weight loss during heating under nitrogen atmosphere was analyzed using a simultaneous thermogravimetric analyzer (METTLER TGA/DSC Pro, Switzerland).The volume resistivity of ECA sample with certain formulation was measured using a four-point probe (MCP-T610, Japan) in-line method. The capacitance of the capacitive touch panel before and after touched was measured using a Victor 9801A+ multimeter.

III. RESULT AND DISCUSSION

A. Characterizations of the Branched Submicron Silver Particles

The morphology and crystallinity of the silver micro-particles are shown in Fig. 1. From the SEM analysis, it can be clearly observed in Fig. 1a that the as-prepared silver particles were of branched structure, with a uniform particle size of about 500 nm. As shown in Fig. 1b and 1c, the silver particles consist of numerous petal-like nanostructures with a thickness less than 20 nm, which indicate excellent low-temperature sintering ability and unique optical characteristic.

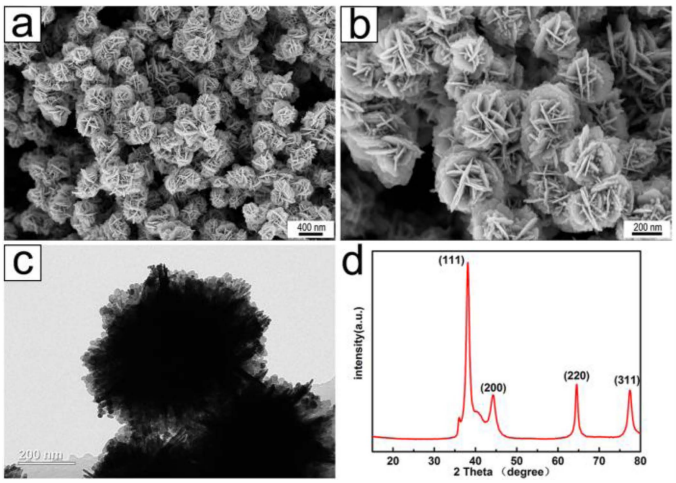

Fig. 1. (a) SEM images of branched submicron silver particles. (b) Magnified SEM images of branched submicron silver particles. (c) TEM images of branched submicron silver particles. (d) XRD pattern of branched submicron silver particles.

The crystalline structure was further examined by the powder XRD analysis. Figure 1d shows the XRD pattern of the branched submicron silver particles with a sharp and strong diffraction peak together with three weak diffraction peaks, which are indexed to the (111), (200), (220), and (311) planes of the face-centered cubic (fcc) crystalline structure, respectively. The intensity ratio of the (111) peak to (200) peaks is 3.88. Compared with the intensity ratio of the standard silver powder pattern (JCPDS card no. 04-0783, 2.1), it can be indicated that the branched submicron silver particles have an obviously preferred orientation along the (111) lattice pattern.

It may be ascribed to a combined effect from the selective adsorption of citrate ions and complexation of hydrazine hydrate.

B. *Effects of Reaction Parameters on Silver Particles*

Studying the effects of reaction parameters is important for controlling the morphology of the reaction product, and for understanding the formation mechanism of branched submicron silver particles. In this reaction system, the pH value of hydrazine hydrate solution and the concentration of the essential reagents ($AgNO_3$, $N_2H_4 \cdot H_2O$) were investigated.

When the concentration of all the reagent remained unchanged, the pH value of hydrazine hydrate solution was adjusted by addition of dilute nitric acid with a series of values of 8, 8.5, 9, 9.5, 10, 10.5, respectively. As shown in Fig. 2, the petal-like nanostructures get thinner with the lower pH value, as well as the increase of nanoplates on the surface of the petal-like nanostructures. It may be due to the weaker reducing ability of hydrazine hydrate. As controlled by reaction kinetic, the lower pH value of the solution makes reducing ability of hydrazine hydrate weaken, so as to inhibit the growth rate of the petal-like nanostructures.

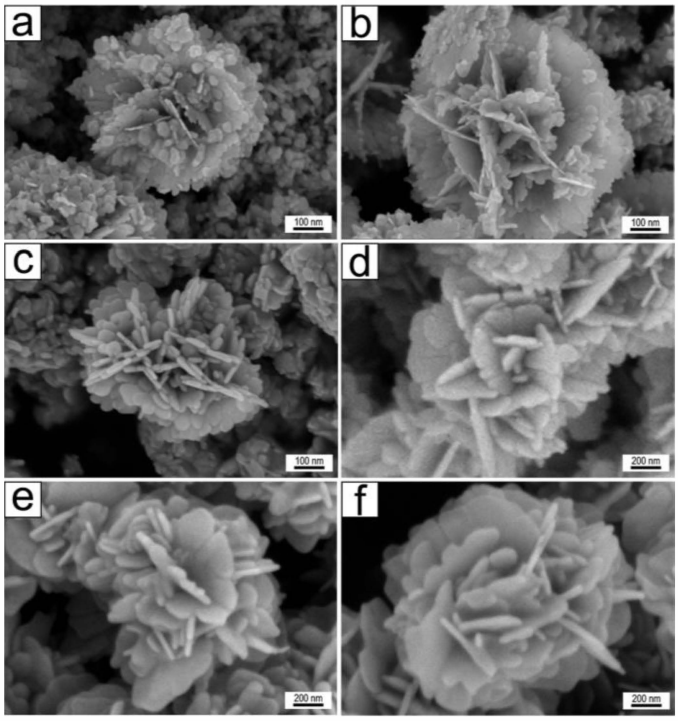

Fig. 2. (a) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 8. (b) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 8.5. (c) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 9. (d) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 9.5. (e) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 10. (f) SEM images of branched silver particles at the $N_2H_4 \cdot H_2O$ with a pH value of 10.5.

Apart from the issue of pH value, the concentration of the reagents can influence the silver products effectively as well. When we increased the concentration of $AgNO_3$ and $N_2H_4 \cdot H_2O$ with the mole ratio fixed in the fabrication to investigate the function of reagents, it can be clearly observed in Fig. 3 that branched silver particles with insignificant change of size were obtained at the concentration of silver nitrate solution ranging from 0.12 M to 0.48 M. When the concentration is significantly increased (Fig. 3b, d and f), there are more petal-like nanostructures formed by abundant silver atoms as a result of the high concentration of silver ions and strong reducing ability of hydrazine hydrate.

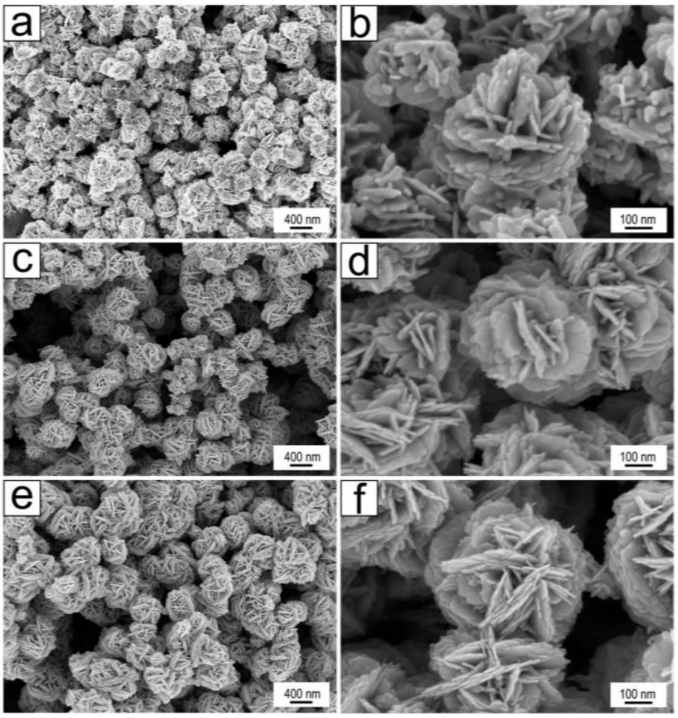

Fig. 3. SEM images of branched silver particles at the $AgNO_3$ and the $N_2H_4 \cdot H_2O$ with different concentration of (a) ~ (b) 0.12M, 0.24M. (c) ~ (d) 0.24M, 0.48M. (e) ~ (f) 0.48M, 0.96M.

According to the above results, the pH value of hydrazine hydrate solution and the concentration of the essential reagents ($AgNO_3$, $N_2H_4 \cdot H_2O$) affect the morphology of the silver particles, as well as the petal−like nanostructures significantly.

C. *Investigation of the Sintering Behavior and Purity of the Branched Submicron Silver Particles*

Although the melt point of bulk silver is about 960 °C, nanostructured silver can achieve a very low sintering temperature due to size-effect [16, 20]. In order to observe and prove the low temperature sintering process of branched submicron silver particles, the samples were annealed at 150 °C for 0.5 h, and the morphologies were analyzed by SEM images (Fig. 4). Compared to the silver submicron particles prepared at room temperature, there are thickened petal-like nanostructures without nanoplates on the surface after annealing at 150 °C, which indicates the low temperature sintering process occurred. it may be favorable to decrease the contact resistance of silver fillers in ECAs. Hence the volume resistivity of 50 wt% ECAs based on branched silver particles are measured, and the value was 1.12×10^{-4} Ω·cm which realized excellent conductivity, which means that the highly branched silver particles render a low percolation threshold.

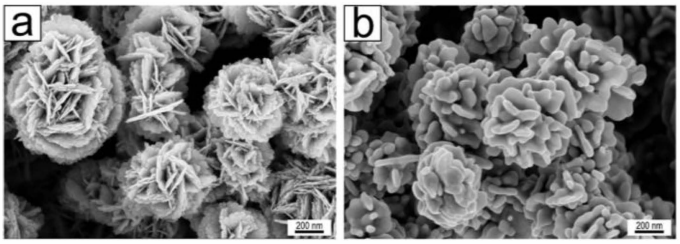

Fig. 4. (a) SEM images of as-prepared branched silver particles at room temperature. (b) SEM images of branched silver particles after annealing at 150 ℃ for 30min.

The as-prepared branched submicron silver particles have a high purity, which was confirmed by Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) in nitrogen environment. As shown in Fig. 5a, there is no strong peak in the curve, which suggests that few remanent reagents exist. The weight loss is less than 1% at 700 °C (Fig. 5b), which can be further suggested that the formed branched submicron silver particles are pure and clean. Differential scanning calorimetry (DSC) analysis of branched silver particles does not give a clear image of the phase change behavior in the ramping temperature range.

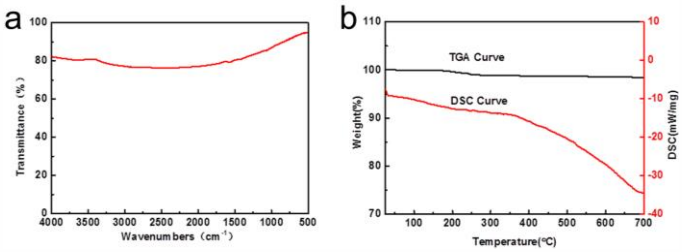

Fig. 5. (a) FTIR of branched submicron silver particles after drying in vacuum. (b) TGA analysis of as-prepared branched silver particles (black line), and DSC analysis of the branched silver powder (red line). The sample was heated from 25 °C to 700 °C in nitrogen at 10 °C /min.

Combining with the above results, we can claim that as-prepared branched silver particles with high purity have the characteristics of low temperature sintering, excellent electrical conductivity and low threshold, which promises broad applications of ECAs in microsystems packaging and printed electronics.

D. the Research of the Potential Applications in Printed electronics

For the feasibility of applications of ECAs in printed electronics, we fabricate two kinds of prototype samples, which include LED arrays and a capacitive touch panel by using branched silver-filled ECAs. As shown in Fig. 6, it is easy to print and cure branched silver-based ECAs as conductive fine tracks on glass and PET. It is obvious seen that six lightened LEDs powered by a regulated DC power supply with a potential of 9V (Fig. 6a). The performance characteric of the capacitive touch panel sample is valued in Fig. 6c and 6d. The touch panel has a capacity of 0.18 nF in air atmosphere. Touching the capacitive panel with finger is equivalent to a capacitor in parallel with the capacitor of human body (~ 100 nF), which makes the total capacitance increase to 4.39 nF. It further indicates that the branched submicron silver-filled ECAs have potential applications in printed electronic components like touch panel, printed capacitor, and so forth.

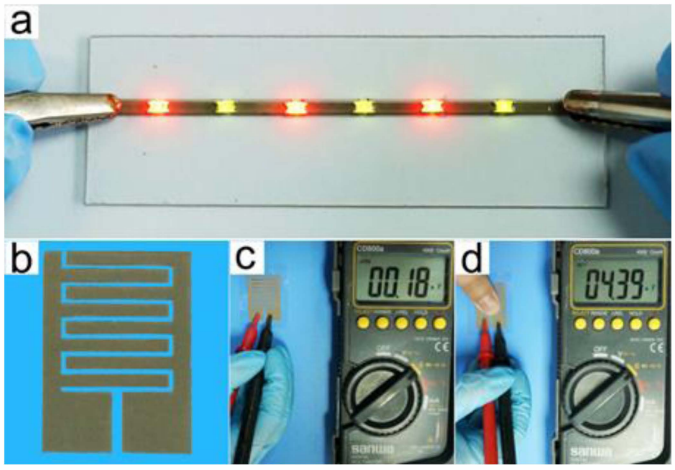

Fig. 6. (a) Photographic image of printed ECAs with attached LEDs on glass. (b) Prototype of capacitive touch panel by screen printing. (c) ~ (d) The capacitance of the capacitive touch panel before and after touched.

IV. CONCLUSION

In summary, we have demonstrated a facile and scalable synthetic method of monodispersed branched submicron silver particles which is about 500 nm in size. The reaction parameters, such the pH value of hydrazine hydrate solution and the concentration of the reagents ($AgNO_3$, $N_2H_4 \cdot H_2O$), can influence the morphology of the silver particles, as well as the petal−like nanostructures significantly. The as-prepared branched silver particles of high purity possess unique petal-like nanostructures of about 20 nm in thickness, which render highly efficient conductive network, percolation threshold and low excellent low temperature sintering ability (about 150 °C). And the ECAs based on these branched submicron silver particles demonstrate a low resistivity, which is 1.12×10^{-4} Ω·cm with a silver content of 50 wt%. Meanwhile, the branched submicron silver particles filled ECAs can be easily printed on glass and PET. The outstanding performances of the LED arrays and the capacitive touch panel enable a large variety of applications in printed electronic devices. Considering the simple, cost-effective, scalable and eco-friendly liquid phase synthetic method, along with above intriguing advantage mentioned, this technology may further find potential applications in microsystems packaging and ultrafine flexible circuits.

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