Scalable Synthesis of the Mono-dispersed Silver Micro-dendrites and Their Applications in the Ultralow Cost Printed Electrically Conductive Adhesives

Xiaoya Cui, Cheng Yang*, Zhexu Zhang, Haoyi Wu, Sumwai Chiang, Zijin Su, Jingping Liu, Feiyu Kang

Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University
Li Shui Road, Nanshan, Shenzhen City, China, 518055
yang.cheng@sz.tsinghua.edu.cn

***Abstract*—Electrically conductive composites have been intensively studied as the interconnects and the printed lines in the next generation of electrical devices. Silver fillers have been widely accepted as the key conductive filler material due to their excellent electrical conductivity, malleability, chemical and mechanical stability. Here we for the first time introduce a scalable synthesis of the mono-dispersed silver dendrites with 3-D micro- and nano- structures, and their uses as the conductive filler for the electrically conductive adhesives (ECAs) with ultralow silver content. These silver dendrites have a unique 3-D fractal structure, which are able to provide excellent low-temperature sintering ability due to the abundant nanostructures at the edge of the dendrite leaves. This feature renders them form excellent electrical percolation network with ultralow concentration (percolation threshold down to 20 wt%) in conventional engineering resins, which is currently the one with the lowest percolation threshold for the micro-metal-filler based ECAs. Thermal analysis (TGA/DSC) and scanning electron microscopy (SEM) suggest that the silver dendrite powders go through a sintering process at the temperature below 150 ºC, thus the adjacent dendrites are able to form effective ohmic conductance. Considering the low materials preparation cost and negligible environmental risk, this method suggests an effective way to develop environmentally benign materials for the flexible printed electronics devices.**

Keywords—silver dendrites; 3-D fractal structure; electrically conductive adhesives; percolation threshold; low-temperature sintering

I. INTRODUCTION

In recent years, there have been numerous works on electrically conductive adhesives (ECAs) which is aimed to replace the conventional eutectic Sn/Pb solders in microelectronics applications [1-3], considering the fact that ECAs can offer many advantages, including environmental friendliness, low processing temperature, low stress on the substrate and simple processing [4-5]. Typical ECAs consist of an epoxy resin matrix filled with electrically conductive fillers. Among various electrically conductive fillers, silver is one of the best choices due to its excellent electrical and thermal conductivities. As an important thermal and electrical conducting material for electronic packing, the silver-filled ECAs have been widely applied in die attachments, solar cell panels, radio frequency identification (RFID) antennas, flexible touch panel interconnects and many other technologies [6-7]. However, the high cost of silver is a major disadvantage which limits wider application of Ag-filled ECAs in microelectronics. Thus the key point is that the electrical conductivity, heat dissipating capability and stability of product must be further improved, and at the same time, the silver content of the ECAs should be decreased so as to reduce the materials cost.

In order to obtain good conductivity in three-dimensions, the silver content of the conventional ECAs must at least reach 50% weight percent [7]. Nowadays, many efforts have been done to develop a set of chemical and physical methods to improve the electrical performance of ECAs, including introducing zero dimensional silver nanoparticles, one dimensional silver nanowires, and two dimensional silver

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microflakes; and there are also surface engineering method studies of the silver fillers. Considering the fact that most of the available ECAs are based on the 2-D silver microflakes and 0-D silver nanoparticles [7-10], one may think of other morphologies which may help further optimize the percolation network. During the past years, dendritic morphology of noble metals (including silver) captured the attention of materials scientists, for their attractive structures and important applications as catalysts and sensing substrates for surface enhanced Raman scattering (SERS) [11-13]. Herein we note that this special 3-D micro- and nano-structure is able to form a uniform percolated network with high efficiency due to the abundant contacting points among the adjacent dendrites. Moreover, the nano-sized tips with the fractal morphology of the dendrite can go through a low temperature sintering process, which is an extra advantage. However, to the best of our knowledge, there were no reports on using the 3-D silver microstructures as the ECAs fillers, which is due to the lack of available preparation methods to obtain mono-dispersed silver dendrites in large-scale.

In this paper, we report a scalable synthesis method of mono-dispersed micro-silver dendrites, via direct mixing of aqueous $AgNO_3$ and NH_2OH solutions at room temperature; and this method has been confirmed to be efficient and reproducible [13]. Through controlling the critical experimental parameters such as molar ratio, concentration of the reactants, and the reaction speed and temperature, we are able to obtain mono-dispersed and uniform silver dendrites with the optimum 3-D fractal structure and size for the ECAs fillers. Also the morphology, structure and SERS enhancement effect of these silver dendrites are characterized. Moreover, through introducing the iodination method to activate the silver dendrites filler surface, the electrical conductivity of ECAs can be further improved. We conducted a series of experiments to study the effect of curing temperature to the bulk resistivity of the silver dendrite based ECA samples with different silver content. As compared with the commercial silver microflakes (percolation threshold of ECA is about 50 wt%), the silver dendrites exhibit a unique character of forming conductive network in ultralow concentrations (percolation threshold down to 20 wt%) in various engineering resins e.g. epoxy resin 828 (Shell). Meanwhile, it was found that the silver dendrite powders go through a sintering process at a relatively low temperature (less than 150 °C), which is an advantage for developing flexible electronics devices.

II. EXPERIMENTAL

A. Materials

Silver nitrate ($AgNO_3$) powder (99%) and ammonium hydroxide NH_2OH solutions (50% aq.) were purchased from Sigma Aldrich and Alfa Aesar, respectively. Bisphenol-A type of epoxy resins and anhydride type of curing agents were supplied by Nanya Epoxy Company.

B. Synthesis of Ag dendrites

Equal volumes of silver nitrate aqueous solution (6 mmol) and of ammonium hydroxide solution (24 mmol) are dropped into a beaker via a double-channels peristaltic pump simultaneously at room temperature. The beaker is gently shaken during the reaction. The precipitate was rinsing with DI water twice and then dispersed in ethanol for further uses.

C. Preparation of ECAs

The electrical resistivity of the printed ECA samples using different curing condition and filler loading were studied. The experimental setup is as follows: firstly, the dispersed dendrites were treated by iodine for surface modification according to procedures as we previous reported [9]. And then we collected the surface modified dendrites using a simple filtration method and dried them in vacuum. A subsequent mixing process was applied to these dendrites with resins and hardeners, and a drop of hexamethylenetetramine (HMTA) was added as catalyze. The ratio of epoxy to hardener was 1:1 by mole ratio based on the epoxide equivalent weight (EEW) of the epoxy resin and the hydroxyl equivalent weight (HEW) of the hardener. We mixed the pastes subsequently in a planetary rotary mixer at 1500 rpm for 12 min. ECA sample with certain formulation is doctor-bladed onto a piece of glass slide by using two parallel scotch tapes (thickness ~90 micron) as the confinement; the gap between the tapes is 2 mm and the length of ECAs is 30 mm. Herein the ECAs with different silver contents were cured at various temperature in a range

from 140 °C to 300 °C. Considering the fact that the curing temperature of epoxy resin is about 150 °C, for those samples curing below 150 °C, the curing time was set to 1 hour; for those samples curing above 150 °C, the curing time was just set to 15 min.

D. Characterization

Resistivity of the ECAs was calculated from bulk resistance of a specimen with specific dimensions. After thermal curing, bulk resistance (R) of ECA strips was measured by a Victor 9801A^{+} multimeter. The thickness of the specimen was measured by the spiral micrometer. Bulk resistivity (ρ) was calculated using equation (1):

$$\rho = \frac{t \times w}{l} \times R \tag{1}$$

where *l*, *w* and *t* are the length, width and thickness of the sample, respectively. Weight loss of the silver dendrites during heating in the nitrogen atmosphere was studied using a thermogravimetric analyzer (NETZSCH SAT 449F3, Germany). The morphology of silver dendrites and polymer nanocomposites was studied by the field emission scanning electron microscopy (FESEM, HITACH S4800, Japan). X-Ray diffraction patterns of silver dendrites were recorded by powder X-ray diffraction (XRD) using a Rigaku diffractometer (D/MAX-2500, Japan) equipped with Cu-Kα radiation. Raman spectra of silver dendrites were recorded by a Jobin-Yvon Horbia 800 using a 532 nm laser.

III. Results and Discussions

A. Characterization of Ag dendrites

Figure 1A shows the low magnification SEM of the silver dendrites. It is obvious that the silver dendrites consist of large quantities of dendritic structures in micro- and nano-range. From the SEM analysis, the dendritic micro-particles are mono-dispersed and are about 5 μm in size. As shown in figure 1B with a high magnification, the silver dendrite consists of regular nano-tip structures. The synthesis of silver dendrite is a process controlled by both reaction kinetics and thermodynamics. High mixing rate and temperature can result in a high reduction rate, so as to accelerate the nucleation and growing speed [14]. The reduction process finished quickly after the mixing of the reactants, and the mono-dispersed and uniform micro- structures were obtained. Nevertheless, the formation mechanism of the silver dendrites needs further investigations.

The dendritic structure was further examined by the powder XRD analysis. Figure 1C shows the XRD pattern of the silver dendrites. The diffraction peaks observed are the (111), (200), (220), (311), and (222) diffraction peaks, respectively, which are the typical peaks of face-centered cubic (fcc) structure of silver. The intensity ratio of the (111) peak to (200) and (220) peaks are 4.74 and 7.40, respectively. Compared with the intensity ratio of the standard silver powder pattern (JCPDS: 2.1 and 4.0, respectively), it can be indicated that the silver dendrites may have an obviously preferred orientation along the (111) lattice pattern [15].

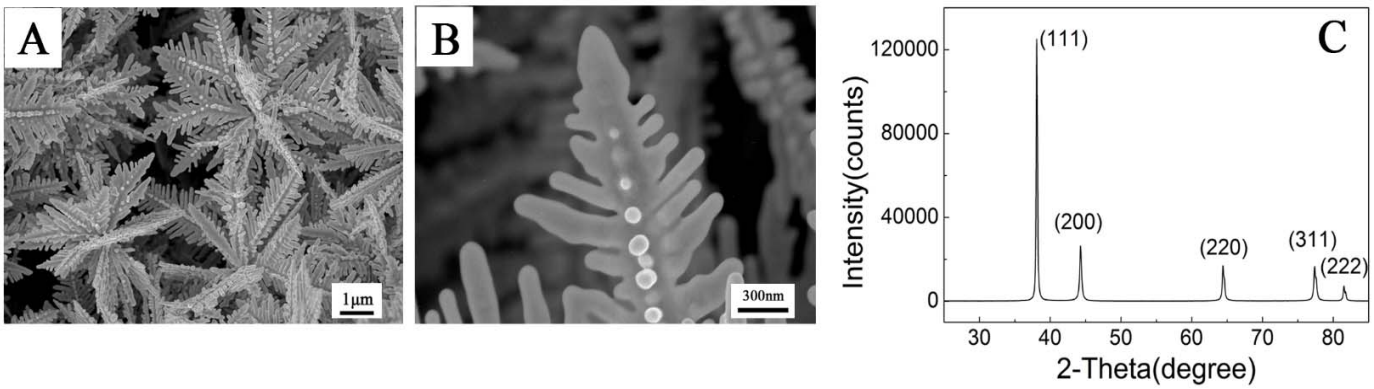

FIGURE 1. Typical SEM images of silver dendrites (A and B correspond to different magnifications); (C) XRD pattern of the as-prepared silver dendrites.

In order to observe the sintering process of the silver dendrites, the samples were annealed at 100 °C, 150 °C, 180 °C, 200 °C, 250 °C and 300 °C for 0.5 h, respectively. The morphologies were analyzed by SEM images, as shown in figure 2. We can see that the secondary structure of every branch is almost kept intact; nevertheless, with the rise of curing temperature, the silver grains on the secondary structure began to transfer to the primary structure, which indicates that the sintering process occurred. When the curing temperature increased to 300 °C (figure 2F), the primary structure changed from dendritic ones to micro- particles, and the microstructure tips of adjacent silver particles seriously sintered with each other. As shown here, the secondary structure of the dendrites disappears at 150 °C (figure 2B), which indicates that the low temperature sintering of the nanostructure of dendritic silver happens.

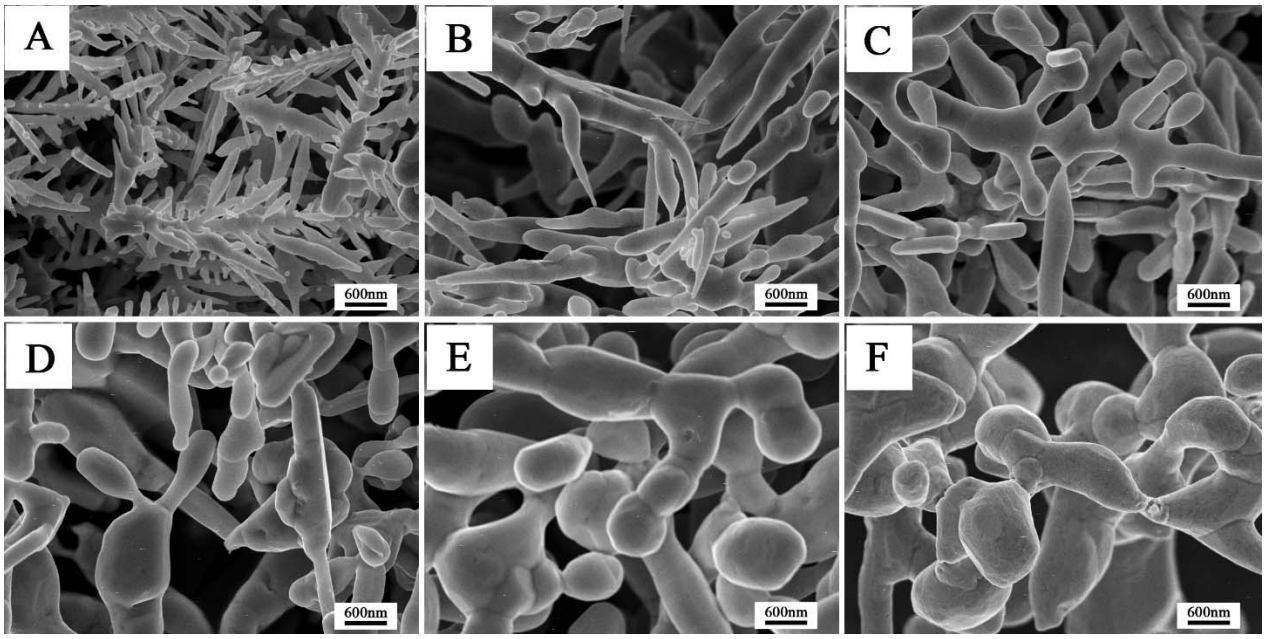

FIGURE 2. SEM images of the silver dendrites after annealing at (A) 100 °C for 0.5h, (B) 150 °C for 0.5h, (C) 180 °C for 0.5h, (D) 200 °C for 0.5h, (E) 250 °C for 0.5h and (F) 300 °C for 0.5 h in Argon.

The as-prepared silver dendrites have excellent thermal stability, which was confirmed by thermal gravimetric analysis (TGA) in nitrogen (figure 3a). The weight loss is less than 0.3% at 500 °C, which can be suggested that only pure and clean silver dendrites are formed. Differential scanning calorimatry (DSC) analysis of the silver dendrites does not give a clear image of the phase change behavior in the ramping temperature range (the valley below 100 °C is due to the flow disturbance of the instrument). Comparing the sintering information from the SEM images (figure 2), we suppose that the silver micro- and nano- structured go through a low temperature (150 °C) sintering process, which is favorable to decrease the contact resistance of silver fillers in ECAs, thus to realize excellent conductivity with low content of silver.

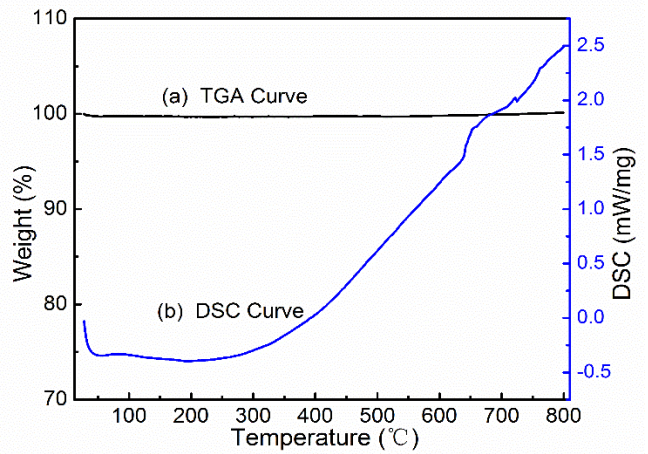

FIGURE 3. (a) TGA analysis of the silver dendrites as-prepared (black line). (b) DSC analysis of the silver dendrites powder (blue line). The sample was ramped from 25 °C to 600 °C in Argon at 5 °C /min.

The silver dendrites were evaluated by the surface enhanced Raman Scattering spectroscopy. Figure 4 displays the SERS spectra of Rhodamine 6G (R6G) on the surface-modified dendritic silver samples. From the spectra, we can observe that the spectrum of the 10^{-7} M R6G treated silver dendrite is dominated by the relatively strong peaks at 1648, 1566, 1508, 1361, 1280, 1197, 1077, 936, 767, 622 and 421cm^{-1}, which practically agreed with the previous report [16]. Considering the fact that the main part of silver dendrite is micro-structured, those nano-tips may play as the "hot spots", which play a key role in the SERS enhancement [16].

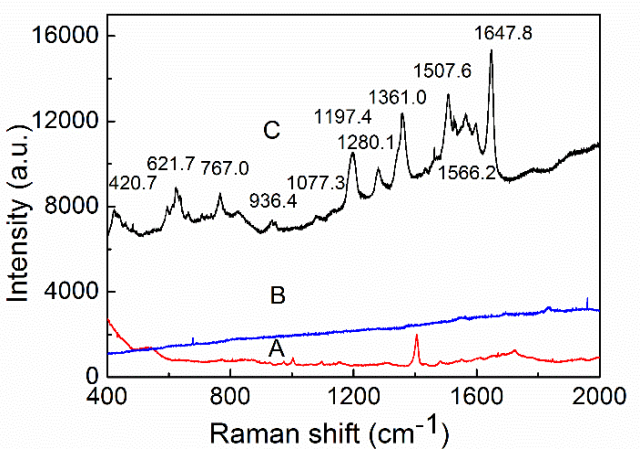

FIGURE 4. Raman spectra of (A) original silver dendrites, (B) R6G solution (1×10^{-7}M), (C) silver dendrites with the chemisorbed R6G (1×10^{-7} M).

B. The effect of curing temperature on the resistivity of ECAs

Figure 5A displays the experimental results of the electrical resistivity data, indicating the effects of curing temperature on the resistivity of the ECAs. As shown here, whereas the content, the resistivity decreases with the increase of curing temperature, the electrical resistivity of 20 wt%, 30 wt%, 40 wt%, 50 wt%, and 60 wt% of the silver fillers are observed, which are 0.05 Ω•cm, 7.36×10^{-3} Ω•cm, 1.79×10^{-3} Ω•cm, 8.32×10^{-4} Ω•cm, and 3.20×10^{-4} Ω•cm, respectively. Due to its high silver content, the 60 wt% samples have the lowest electrical resistivity at about 10^{-4} Ω•cm, except for the sample of curing temperature at 140 °C, which is below the hardening temperature of resin. Therefore, we tentatively elongated the curing time up to 1 h, yet an increase of the resistivity occurred, correspondingly, which may be related to the oxidation problem. When the silver content is decreased to 30 wt%, the samples can keep a good electrical resistivity at 10^{-3} Ω•cm as well. Moreover, when the silver content is down to 20 wt%, the ECAs are still conductive. By contrast, the percolation threshold of ECAs with silver flake as fillers can just reach 27.5 wt% [9], so the silver dendrites show a marked advantage as the ECA filler. It is also worth mentioning that when the curing temperature is higher than 240 °C, the ECAs becomes nonconductive. This is due to the serious sintering of the silver dendritic fillers, and the morphology changes severely (figure 2E), thus it is unable to support the fillers to build up a percolated network.

Figure 5B and C are the surface morphology images of the ECAs solidified at 150 °C for 15 min with various silver contents. For the silver dendrites are 3-D structured, the surface images are able to provide information about the silver dendrites distributed inside the epoxy resin. As shown in figure 5, the 20 wt% ECA can realize a tip-to-tip contact model among the adjacent dendrites. With the silver content increases, the contact areas become larger; when the content rises to 60 wt%, the tips sintered more severely, forming prominent necking. It effectively reduces or even eliminates the contact resistance among the silver dendritic fillers, and enables the formation of a 3-D conductive network within the polymer matrix. To sum up, the percolation threshold of ECA with silver dendrites as fillers can be lowered down to 20 wt%, and the optimum curing temperature is about 200 °C, which is depended on the silver content. The electrical resistivity of ECA with 20 wt% silver content is about 0.01-0.1 Ω•cm below 240 °C. We believe that if the ECA process parameters are further optimized, the conductivity is able to be improved remarkably.

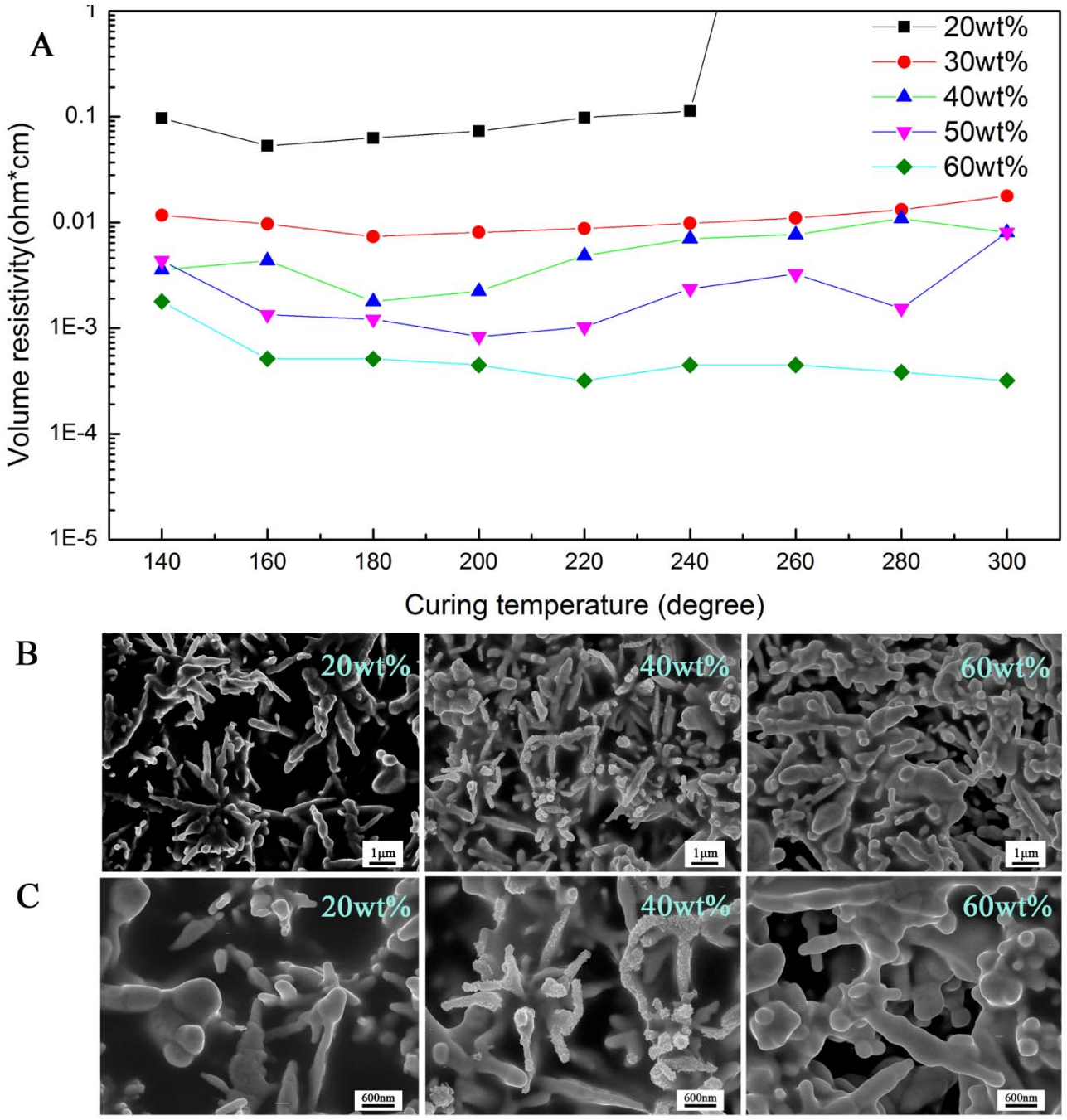

FIGURE 5. (A) The volume resistivity of the modified ECAs and controlled with different silver contents after different curing temperature; SEM images of the surface of ECA solidified at 150 °C for 15 min with various silver content, (B) the scale bar is 1 μm, and (C) the scale bar is 600 nm.

IV. CONCLUSIONS

We have demonstrated a scalable synthesis of the mono-dispersed silver dendrites with 3-D micro- and nano-structures. Its unique 3-D fractal structure can provide the low temperature sintering ability due to the abundant nano-tips at the edge of the dendrite branches, which is favorable to making conductive fillers for the electrically conductive adhesives (ECAs) with ultralow silver content (percolation threshold is lowered down to 20 wt% in a conventional engineering resin). The electrical resistivity of 20 wt%, 30

wt%, 40 wt%, 50 wt%, and 60 wt% of the silver fillers are observed, which are 0.05 Ω•cm, 7.36×10^{-3} Ω•cm, 1.79×10^{-3} Ω•cm, 8.32×10^{-4} Ω•cm, and 3.20×10^{-4} Ω•cm, respectively. The curing temperature of ECAs affects the resistance, and the optimum curing temperature of ECA is about 200 °C, which depends on the silver content. The electrical resistivity of ECA with 20 wt% silver content is about 0.01-0.1 Ω•cm below 240 °C, which indicates that we can manage a low curing temperature and low filler content of an ECA. Thermal (TGA/DSC) and scanning electron microscopy (SEM) analyses suggest that the silver dendrite powders go through a sintering process at the temperature under 150 °C, thus the adjacent dendrites are able to form effective ohmic conductance. Considering the low materials preparation cost and negligible environmental risk during preparations, this method suggests an effective way to develop environmentally benign materials for the flexible printed electronics devices.

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