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Highly Conductive and Stretchable Ag Nanodendrite-Based Composites for Application in Nanoelectronics

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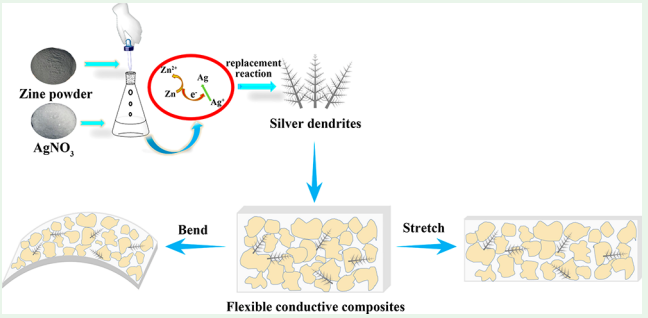
Supporting Information

ABSTRACT: Stretchable flexible conductive composites have received considerable attention recently. In this study, highly conductive and stretchable composites were synthesized using Ag microflakes (AgMFs), Ag nanodendrites (AgNDs), and thermoplastic polyurethane (TPU). The AgNDs are prepared by a facile replacement reaction between silver nitrate and zinc powder. The AgMFs/AgNDs/TPU flexible conductive composites show excellent electrical (8.28×10^{-5} Ω·cm), mechanical, and flexible properties, which can be bent, twisted, and stretched (elongation at break is as high as 250%). During the deformation process, the AgNDs act as conducting bridges between AgMFs. This resulted in good conductive stability of flexible conductive composites under bending, twisting, and stretching. The significant electromechanical properties are also demonstrated by a simple flexible circuit composed of a light-emitting diode (LED) and the stretchable conductor. The AgMFs/AgNDs/TPU flexible conductive films were bent or twisted 10000 times, and the LED can still work well. Taken together, the AgMFs/AgNDs/TPU flexible conductive composites with outstanding electrical and mechanical properties are especially suitable for the flexible electronics device applications.



KEYWORDS: *silver nanodendrites, replacement reaction, stretchability, conductivity, AgMFs/AgNDs/TPU, flexible electronics*

INTRODUCTION

The need for flexible and stretchable electronic devices has become extraordinarily urgent with the rapid development of information and intelligent technology. Compared with conventional rigid electronic devices, stretchable devices that can be stretched, bent, and twisted provide users with more functions and open up many new applications, such as wearable electronic devices,[1−4] flexible and conformal antennas,[5,6] flexible displays,[7,8] flexible supercapacitors,[9,10] sensors,[11−14] flexible electronic circuits and electrodes,[15] and flexible solar cells.[16] A challenge in making stretchable electronics is the development of stretchable conductors that possess good conductivity, flexibility, and stretchability.[17] Recent progress on stretchable conductors with good performance is based on two kinds of approaches. One is to incorporate conductors having specially shaped structures, such as wavy, relaxed, and net-shaped structures, into elastic polymers for prestoring strains.[18−21] The other is mixing a conducting material with an elastomer to make elastic conductive composites that can sustain a strain.[22−26] The former has limits in terms of the anisotropic stretchable properties, and the fabrication process required for flexible inorganic materials is typically complex.[27] The latter provides isotropically stretchable materials, and the fabrication processes are very simple.

To realize excellent performance of stretchable conductors, many efforts have been made to research all kinds of conductive materials such as carbon nanotubes,[28] graphene,[29] or metal nanomaterials.[30] The carbon nanomaterials have relatively low electrical conductivity; a high loading of carbon materials was necessary to obtain a highly conducting composite. However, incorporation of high concentrations of carbon materials into an elastic polymer increases the stiffness of the resulting composite and decreases its stretchability.[31] Among the metal nanomaterials, silver nanowires (AgNWs) have shown promising application as conductive fillers in stretchable conductors or transparent conductive films due to their excellent electrical properties, moderate oxidation stability, and high aspect ratio.[32] In recent years, AgNDs with fractal structure have gained wide attention. AgNDs have not only a high aspect ratio but also beautiful and intriguing micro-/nanostructures. This means that the AgND is a

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potential conductive filler because it has abundant contact points, which make it easier to form conductive networks. In addition to single conductive filler, hybrid materials are also applied to stretchable conductors. For example, numerous hybrid fillers containing different dimensional nanostructures were developed to control the morphology of conductive network due to their synergistic effect.[33,34] Lee et al.[15] reported the fabrication of stretchable conductive fiber by embedding silver nanowires (AgNWs) and silver nanoparticles (AgNPs) into a styrene−butadiene−styrene (SBS) elastomeric matrix. When the content of silver was 0.56 wt %, the electrical conductivity of the composite fiber was 2450 S cm^{-1} and the elongation at break was 900%. However, when too many AgNWs were mixed in the SBS solution, the AgNWs would be aggregated with each other, resulting in poor dispersion in polymer substrate, which lowers the electrical conductivity. To solve the agglomeration problem of AgNWs, Lu et al.[35] reported surface-modified AgNWs with poly(ethylene glycol) (PEG) derivative to improve the dispersibility of AgNWs. Although the maximum mass fraction of AgNWs in the conductive composite was 75.9 wt % and its electrical conductivity was as high as 14205 S cm^{-1}, the experimental process was relatively complex.

In this work, highly conductive and stretchable flexible composites were fabricated by mixed AgMFs and AgNDs into a TPU matrix. The AgNDs were prepared by a facile replacement reaction.[35] The mixture of AgNDs and AgMFs can provide more electrical pathways in the TPU matrix and enhance the conductivity of flexible conductive composites. In addition, AgND could be a bridge in the cracked regions while being subjected to large deformation because of its large aspect ratio. Therefore, the AgMFs/AgNDs/TPU flexible conductive composites may exhibit excellent conductive property and electrical stability under various mechanical deformations. It is possible for the excellent material properties to make the practical application of the AgMFs/AgNDs/TPU composites in flexible devices.

EXPERIMENTAL SECTION

Materials. Zine powder was obtained from Tianjin Fuchen Chemical Reagents Factory (~20 μm). Silver nitrate was purchased from Xi'An Chemical Corporation. The silver flakes (irregular sheet structure, size 5−20 μm) were supplied by Strem Chemicals, Inc. Hydrochloric acid (HCl, 38%), ethanol, and *N*,*N*-dimethylformamide (DMF) were obtained from Tianjin Fuyu Fine Chemical Co. Ltd. Nitric acid (HNO_3, 65−68%) was obtained from Chengdu Kelong Chemical Reagent Factory. Thermoplastic polyurethane (TPU) was supplied by Shandong Meirui Material Co. Ltd. All chemicals and reagents of analytical grade or above were used without further purification.

Synthesis of Ag Nanodendrites (AgNDs). The AgNDs were prepared by the conventional replacement reaction.[36] The zinc powder was first treated with hydrochloric acid to remove surface contamination and rinsed with deionized water. 0.1 g of treated zinc powder was dispersed into 10 mL of ethanol and then ultrasonicated for 30 min. A solution of 30 mM silver nitrate was prepared by dissolving 0.204 g of $AgNO_3$ in 40 mL of deionized water. When the silver nitrate was completely dissolved, 2 mL of zinc suspension was added slowly under the stirring conditions. The whole reaction was performed at room temperature and ambient pressure. After stirring for 6 h, the product was washed with deionized water and ethanol in sequence and dried with nitrogen. Finally, the product was collected for characterization.

Preparation of AgMFs/AgNDs/TPU Flexible Conductive Composites. The flexible conductive composites were fabricated with AgMFs, AgNDs, DMF, and TPU. The designed strategy for the fabrication of the flexible conductive composites is illustrated in Figure 1. First, TPU particles were melted in *N*,*N*-dimethylformamide

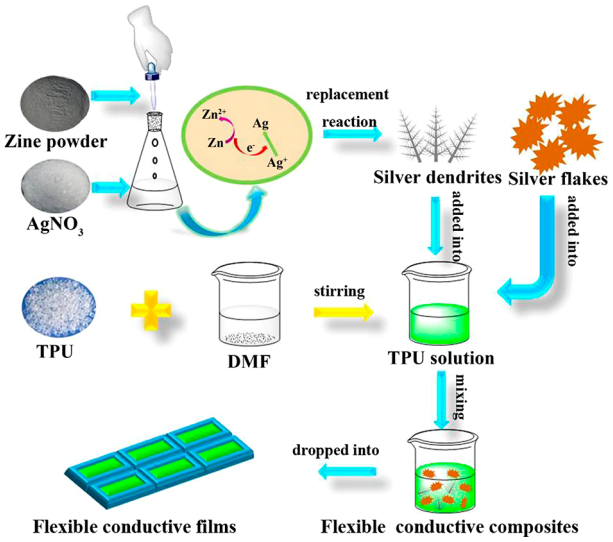

Figure 1. Schematic of the fabrication process of the flexible conductive films.

(DMF) solution with mechanical stirring for 2 h and then kept overnight to remove air bubbles. The AgMFs and synthesized AgNDs were added into the TPU solution. Then, the solution was mixed through a vortex mixer (rotational speed is 2500 rpm) for 1 h to realize the uniform dispersion of the conductive filler. Two strips of polyimide tape were applied onto a precleaned glass slide with a gap width of 3 mm, and the mixed composite was bladed uniformly into the gap between the two strips. The samples were thermally cured at 150 °C for 2 h.

Preparation of AgMFs/AgNDs/TPU Flexible Conductive Films. To test the flexibility of the conductive composites, conductive films were prepared. The flexible conductive composites were dropped into a polytetrafluoroethylene (PTFE) mold (30 mm × 5 mm × 0.5 mm) and scraped smooth to prepare the flexible conductive films. Finally, the films were thermally cured at 150 °C for 2 h.

Characterization. The AgNDs morphology was characterized using a scanning electron microscope (SEM) (JSM-6490LV) from JEOL, and transmission electron microscopy (TEM) images were performed on a FEI Tecnai G20 transmission electron microscope. The X-ray diffraction (XRD) patterns of the samples were obtained using a Bruker D8 advanced X-ray diffractometer, which was used to detect the crystalline structure of the silver dendrites. The resistivity of the flexible conductive composites was measured using a RTS-8 four-point probe meter (Guangzhou four-probe electronic technology, Limited Liability Co.). The resistivity ρ was calculated using eq 1:

$$\rho = R_L \times T \quad (1)$$

where R_L and T are sheet resistance and thickness of the sample, respectively. The thickness of samples was measured by the thickness gauge (Shanghai Chuanlu Measuring Tool Limited Liability Co.). The resistance of the flexible conductive films during bending, twisting, or stretching was measured using a Keysight 34461A multimeter.

RESULTS AND DISCUSSION

Characterization of AgNDs. Figure 2 shows a typical AgNDs structure synthesized by zinc powder and $AgNO_3$ in aqueous solution. From Figure 2A, we can see that a large number of treelike silver structures appeared, which indicates that the AgNDs were successfully prepared. Figure 2B presents

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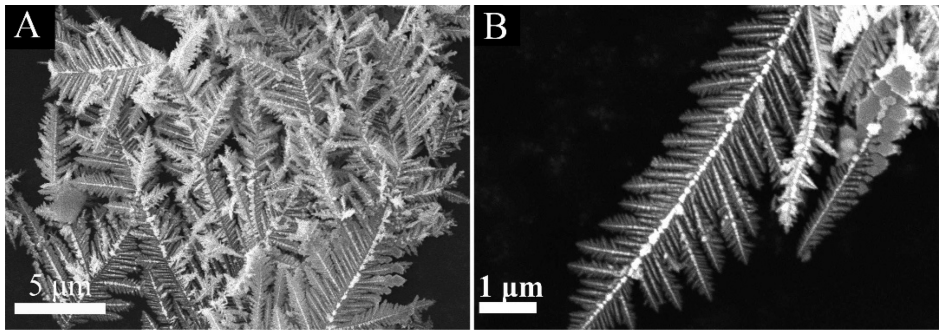

Figure 2. SEM images of silver dendrites: (A) low-magnification SEM image; (B) higher-magnification SEM image.

a high-magnification SEM image of AgNDs. It can be found that the individual dendrite consists of a pronounced central trunk as well as rows of branches and leaves. Each of the branches or leaves in the same row is parallel to each other emerging at ~60° with respect to their trunk. The overall length of the dendrite is about 5−10 μm, the branch is 1−2 μm, and the leaf is 100−300 nm. Figure 3 is the XRD pattern

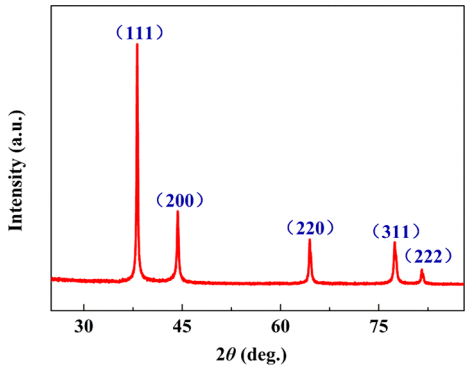

Figure 3. XRD patterns of the synthesized silver dendrites.

of the as-prepared AgNDs, which indicates that the samples are of high crystallinity. The five diffraction peaks can be indexed to the (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) silver (JCPDS No. 04-783).[37,38]

Electrical Properties of AgMFs/AgNDs/TPU Flexible Conductive Composites. The resistivity of AgMFs/AgNDs/TPU flexible conductive composites changing trend under different contents of AgNDs is shown in Figure 4. The total mass fraction of conductive filler is kept at 50 wt %. When AgMFs are used as single conductive filler, the resistivity of the flexible conductive composites AgMFs/TPU is 1.30×10^{-4} Ω·cm. From Figure 4 we can see that the conductive properties of flexible conductive composites are increased by adding AgNDs. When the mass fraction of AgNDs in flexible conductive composites is 0.8 wt % the resistivity reached the minimum value of 8.28×10^{-5} Ω·cm. The results above indicate that AgNDs as fillers can improve the electrical conductivity of the flexible conductive composite with low loading of silver fillers.[35,39]

In this study, we fabricated the AgMFs/AgNDs/TPU flexible conductive composites. The results display a high electrical conductivity. We further investigated the resistance variation of the composites in the bending, twisting, and stretching deformation cycle tests. In the following tests, the AgMFs/AgNDs/TPU conductive film was all with 0.8 wt % AgNDs and 49.2 wt % AgMFs.

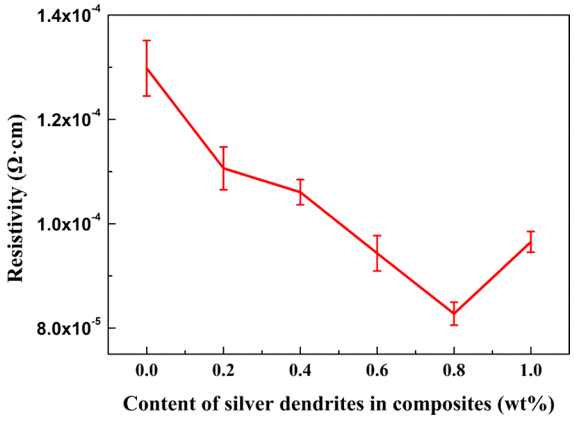

Figure 4. Effect of the content of silver dendrites on the resistivity of flexible conductive composites.

Bending Properties Test of AgMFs/AgNDs/TPU Flexible Conductive Composites. Figure 5 shows the

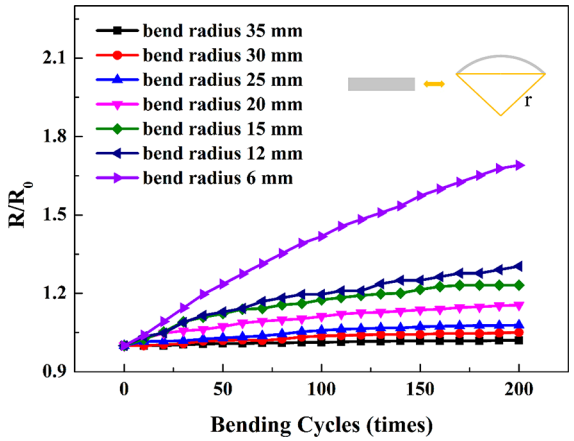

Figure 5. Normalized resistance (R/R_0) of AgMFs/AgNDs/TPU flexible conductive composites as a function of cycles for a bend radius of 35, 30, 25, 20, 15, 12, and 6 mm.

resistance variation (R/R_0) of the AgMFs/AgNDs/TPU flexible conductive composites under bending deformation. A digital multimeter (Keysight 34461A) was used to measure the resistance. R_0 represents the original resistance of the conductive films. R represents the resistance of the film after bending cycle. The flexible conductive films were bent cycle 200 times at the bending radius of 35, 30, 25, 20, 15, 12, or 6 mm.

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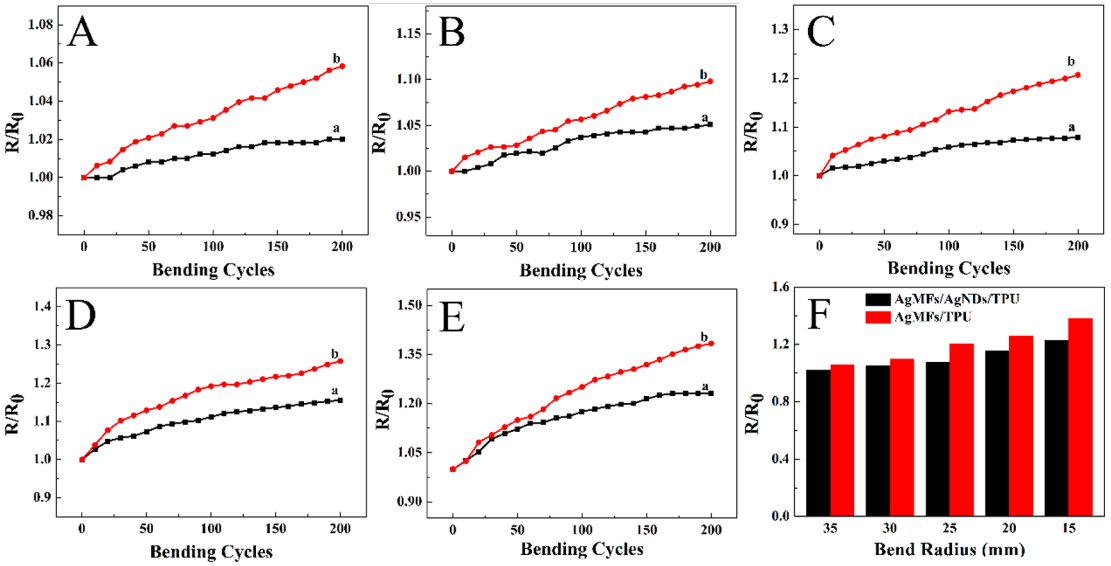

Figure 6. Comparison of normalized resistance (R/R_0) between (a) AgMFs/AgNDs/TPU and (b) AgMFs/TPU flexible conductive composites during bend cycling; the corresponding bending radius is (A) 35, (B) 30, (C) 25, (D) 20, and (E) 15 mm. (F) Normalized resistance contrast histogram of two conductive films of AgMFs/AgNDs/TPU and AgMFs/TPU during bending.

As shown in Figure 5, the normalized resistance R/R_0 is only increased to 1.02, 1.05, and 1.08 after 200 bending cycles at bending radius 35, 30, and 25 mm, respectively. It is noteworthy that the resistance of the AgMFs/AgNDs/TPU flexible conductive composites is still very stable with an increase the degree of bending deformation. For example, when the bending radius is reduced to 20, 15, and 12 mm, the corresponding normalized resistance is 1.16, 1.23, and 1.30 after 200 bending cycles. To further study the electrical properties of AgMFs/AgNDs/TPU under large deformation, we continue to reduce the bending radius. When the bending radius is 6 mm, and the corresponding normalization resistance is 1.69. After the bending cycles, the flexible conductive films can completely recover their original shape without mechanical failure. The above results show that the resistance of the AgMFs/AgNDs/TPU composites under bending cycles was very stable; even at up to 200 bending cycles only a slight increase in normalized electrical resistance was observed.

Bending cycle abilities of flexible conductive composites with different fillers (AgMFs/AgNDs and AgMFs) are compared in Figure 6. The flexible conductive composites without AgNDs provided the highest resistance change upon bending. With the addition of AgNDs, the resistance change trend of flexible conductive composites becomes slower. This demonstrates the excellent role of AgNDs in maintaining conductivity during bending. The stable resistance after bending cycles revealed the excellent electromechanical stability of AgMFs/AgNDs/TPU and their great potential for high-performance flexible conductors.[40]

Twisting Properties Testing of AgMFs/AgNDs/TPU Flexible Conductive Composites. To study the electrical properties of the AgMFs/AgNDs/TPU flexible conductive composites after twisting cycles, the samples were twisted at different angles (30°, 60°, 90°, 120°, 150°, 180°, and 210°). The testing results are displayed in Figure 7. When the twisting angle is 30°, 60°, and 90°, the resistance change is not obvious, and the corresponding normalized resistance is 1.07, 1.18, and 1.29, respectively. This indicates that the AgMFs/AgNDs/TPU flexible conductive composites have good conductivity

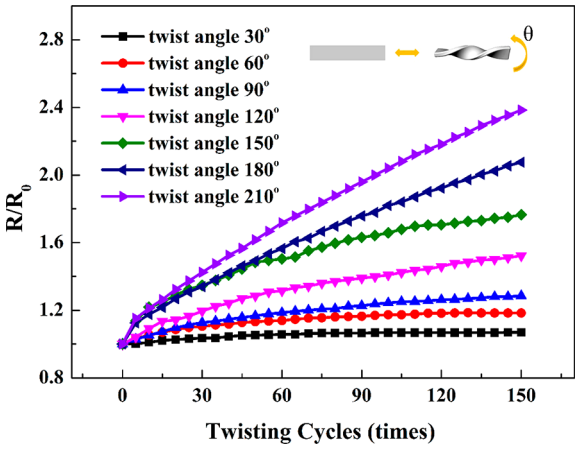

Figure 7. Normalized resistance (R/R_0) of AgMFs/AgNDs/TPU flexible conductive composites as a function of cycles for a twist angles of 30°, 60°, 90°, 120°, 150°, 180°, and 210°.

stability during the twisting cycle. If the twist angle increases, the normalized resistance will gradually increase. As the twisting angle increase to 210°, the normalized resistance is 2.38 after 150 twisting cycles. The increase of resistance is possibly due to the part loss of contact between conductive filler after the mechanical deformations.[38] In addition, from the above results, we can see that twisting has a greater influence on resistance than bending.

Figure 8 shows the difference of normalized resistance between AgMFs/AgNDs/TPU and AgMFs/TPU flexible conductive composites in the twisting cycle. It can be seen from Figure 8A–E that the resistance of flexible conductive composite AgMFs/TPU varies more significantly than that of AgMFs/AgNDs/TPU during twisting cycles. The difference between the normalized resistance of AgMFs/AgNDs/TPU and AgMFs/TPU can be seen more intuitively by the histogram of Figure 8F. The normalized resistance of two samples is little different when the twisting angle is small. But with the increase of twisting angle, the difference in normalized resistance becomes more pronounced. This shows that the

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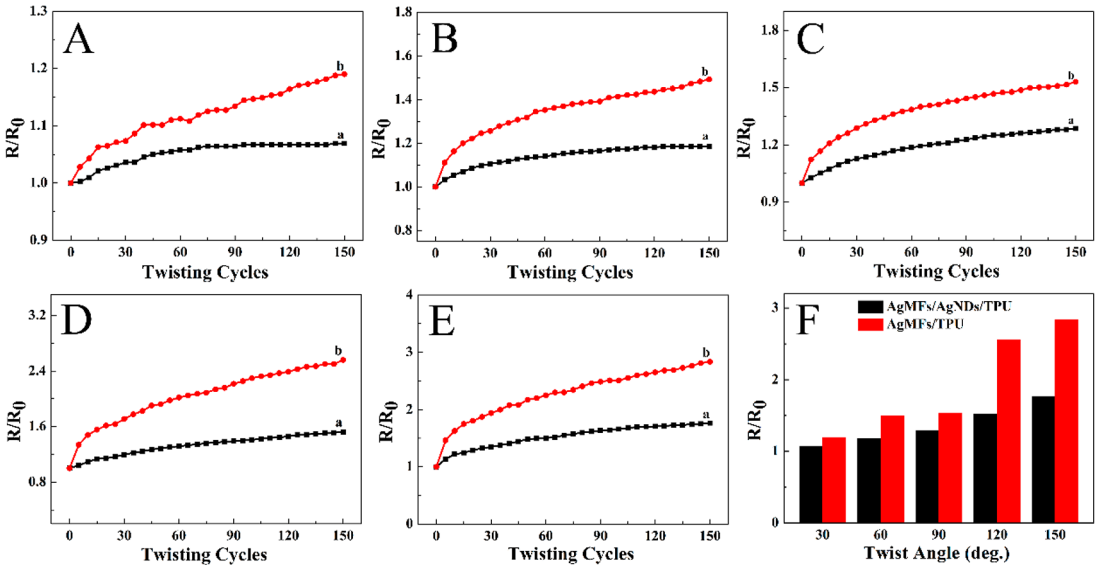

Figure 8. Comparison of normalized resistance (R/R_0) between (a) AgMFs/AgNDs/TPU and (b) AgMFs/TPU flexible conductive films during twist cycling; the corresponding twisting angle are (A) 30°, (B) 60°, (C) 90°, (D) 120°, and (E) 150°. (F) Normalized resistance contrast histogram of two conductive films of AgMFs/AgNDs/TPU and AgMFs/TPU during twisting.

AgNDs is beneficial to improve the conductive stability of flexible conductive composites, and the effect is more obvious under large deformation.[41]

Tensile Properties Test of AgMFs/AgNDs/TPU Flexible Conductive Composites. In addition to the good flexibility, the AgMFs/AgNDs/TPU flexible conductive composites also have excellent tensile properties. The elongation can be as high as 250%. The stretching process is shown in Video S1 (Supporting Information).

Figure 9 presents the results of the stretching cycles of the AgMFs/AgNDs/TPU flexible conductive films with a strain of

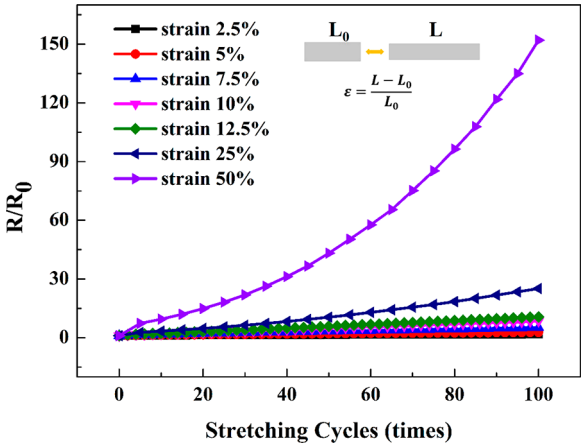

Figure 9. Normalized resistance (R/R_0) of AgMFs/AgNDs/TPU flexible conductive composites as a function of cycles for a set strain of 2.5%, 5%, 7.5%, 10%, 12.5%, 25%, and 50%.

2.5%, 5%, 7.5%, 10%, 12.5%, 25%, and 50%. The resistance increases slightly after 100 cycles when elongations were 2.5%, 5%, 7.5%, 10%, and 12.5%. When the elongation is 25%, the resistances of samples increase with the stretching cycles increase. After 100 stretching cycles, the normalized resistance is 25. To understand the effect of larger deformation on the electrical properties of flexible conductive films, the elongation increased to 50%. At this time, the resistance increases obviously. After 100 stretching cycles, the normalized resistance is 152. The increase of the resistance of the flexible conductive films after stretching cycles possibly attributed to the reorientation of the conductive filler and the increase in the internal filler distance after stretching.[38] Larger strain results in greater distance between conductive fillers, which leads to a greater change of resistance during stretching cycles.[42,43]

The normalized resistances of the AgMFs/AgNDs/TPU and AgMFs/TPU flexible conductive composites are compared in Figure 10. It can be seen from the figure that during the stretching cycles, the normalized resistance of flexible conductive composites AgMFs/TPU increased more obviously than that of AgMFs/AgNDs/TPU. This shows that AgMFs/AgNDs/TPU film has better electrical stability than AgMFs/TPU during the tensile process.

These above results reveal that the AgMFs/AgNDs/TPU composites could be used as excellent conductors with high electrical conductivity. Meanwhile, the AgMFs/AgNDs/TPU conductive composites exhibit excellent flexibility, stretch ability, and electrical stability under various mechanical deformations.

It is speculated that the flexible conductive composites AgMFs/AgNDs/TPU have good electrical properties and conductivity stability mainly related to the existence state of the conductive fillers AgMFs and AgNDs in the matrix. To explore the mechanism of improving electrical properties of flexible conductive composites after adding AgNDs, we observed the SEM images of the AgMFs and AgNDs inside the flexible conductive films before and after deformation (Figure S2). It can be seen from Figure S2A that when the flexible conductive film AgMFs/TPU is in a flat state, the AgMFs are uniformly dispersed in the matrix, and they are interconnected to form conductive paths. Therefore, the AgMFs/TPU film can transfer electrons. When the flexible conductive film AgMFs/TPU is bent (the bending radius is 6 mm), the distance between AgMFs increased, and a part of the conductive networks is broken (Figure S2B). Similarly, when the conductive film is stretched (the strain is 10%), cracks

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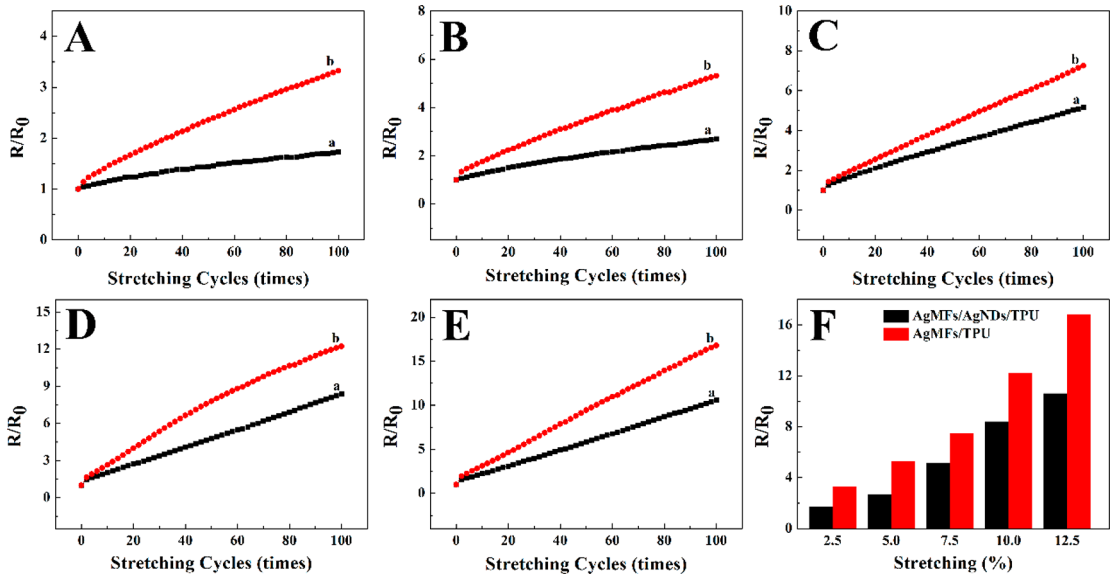

Figure 10. Comparison of normalized resistance (R/R_0) between (a) AgMFs/AgNDs/TPU and (b) AgMFs/TPU flexible conductive composites during stretch cycling; the corresponding elongation are (A) 2.5%, (B) 5%, (C)7.5%, (D) 10%, and (E) 12.5%. (F) Normalized resistance contrast histogram of two conductive films of AgMFs/AgNDs/TPU and AgMFs/TPU during stretching.

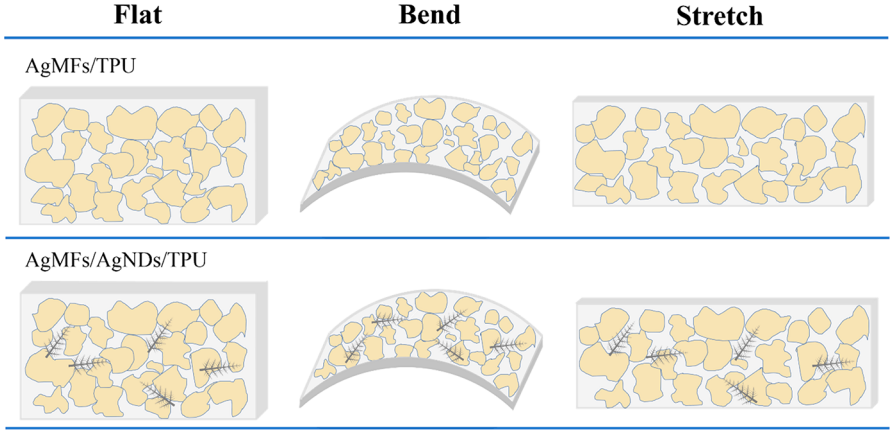

Figure 11. Schematic diagram of flexible conductive films AgMFs/TPU and AgMFs/AgNDs/TPU during flat, bend, and stretch deformations.

appear and the distance increases among the AgMFs (Figure S2C). Therefore, the resistance increases when the flexible conductive film AgMFs/TPU is deformed. To reduce the effect of deformation on the electrical properties of flexible conductive film AgMFs/TPU, a new flexible conductive composite was prepared by adding a small amount of AgNDs into the AgMFs/TPU. Figure S2D–F is an SEM image of flexible conductive film AgMFs/AgNDs/TPU in the flat state. AgMFs and AgNDs can be seen in the low-magnification SEM image (Figure S2D). From the high-magnification SEM image (Figure S2E,F), we can see more clearly the existence state of AgNDs, which are connected between the AgMFs, and a more conductive network is formed. As a result, the resistivity of the flexible conductive composites decreases with the addition of AgNDs. From Figure S2G–I, it can be seen that when the flexible conductive film AgMFs/AgNDs/TPU is bent (the bending radius is 6 mm), the AgNDs act as a bridge connecting adjacent AgMFs, which reduces the damage of bending to conductive network. When the flexible conductive film AgMFs/AgNDs/TPU is stretched (the strain is 10%), it is apparent that the AgNDs are spanning over the gap between two AgMFs and forming a conductive pathway (Figure S2J–L). This allows the flexible conductive film AgMFs/AgNDs/TPU to have better conductivity stability than AgMFs/TPU. Therefore, AgMFs and AgNDs can be used together to improve flexible conductive composites performance as stretchable conductors.

According to the SEM images of the flexible conductive films (Figure S2), we present the existence state of AgMFs and AgNDs in the TPU matrix in Figure 11. From the schematic diagram, we can see the effect of deformation on conductive fillers more intuitively. When the flexible conductive film AgMFs/TPU is deformed, there are many gaps between AgMFs. When a small amount of AgNDs is added, AgNDs can fill the gap between adjacent AgMFs and reduce the effect of deformation on the conductive network. This study demonstrates that construction of a stable conductive network in the matrix is critical to the conductive stability of flexible conductive composites.[44−46] The fractal structure with high aspect ratio and large specific surface area is beneficial to the construction of the conductive network.[39] Therefore, addition

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of AgNDs as conductive filler can improve the electromechanical properties of flexible conductive materials.

In this study, in addition to TPU as the matrix, we also prepared flexible conductive composites by adding AgNDs and AgMFs into poly(vinyl alcohol) (PVA), and its electrical and mechanical properties are studied in the Supporting Information.

AgMFs/AgNDs/TPU Flexible Conductive Composites as Interconnection Materials. A circuit containing a commercial light-emitting diode (LED) was fabricated with as-prepared AgMFs/AgNDs/TPU flexible conductor as connecting wire. Under external electric field, the LED is lightened. Figure S3 shows the condition of the LED lamp under bending of the flexible conductive film. The pictures show that the brightness of the LED lights exhibited almost no change after bending the AgMFs/AgNDs/TPU flexible conductive films to a bend radius of 15 mm under constant voltage. From Figure S4, the LED light is still on when the flexible conductive film is twisted. The LED lights show almost no variation after twisting the conductor to the angle of 180°. This indicates that the AgMFs/AgNDs/TPU flexible conductive composites exhibit good electrical conductivity under bending and twisting.[47,48] In addition, the flexible conductive film has good mechanical durability. The LED lamp will still be able to shine normally when composites are bent or twisted for 10000 times.

A series circuit was fabricated to test the conductive stability under high stretchability by integrating a LED with the AgMFs/AgNDs/TPU flexible conductive films. In Video S2, we can see the brightness changes of the LED lamp during the stretching process. When the elongation of the conductive film is <100%, the brightness of the LED light remains unchanged, and if the flexible conductive film continues to stretch, the LED light will gradually darken. When the elongation reaches 160%, the LED light basically does not shine. Figure S5 shows photographs of the illuminated LED without strain and 100% strain. The images were taken at the same angle under the same backlight illumination condition. As can be seen in the photographs, the LED can still work even under 100% strain, illustrating the high stretchability of the AgMFs/AgNDs/TPU flexible conductive film.

CONCLUSIONS

In summary, highly conductive flexible composites are synthesized by the combination of Ag microflakes (AgMFs), Ag nanodendrites (AgNDs), and the thermoplastic polyurethane (TPU) matrix. The silver dendrites are fabricated through a replacement reaction. The AgMFs/AgNDs/TPU flexible conductive composites exhibit excellent electrical and mechanical properties. When 49.2 wt % AgMFs and 0.8 wt % AgNDs were filled in the TPU matrix, the composite exhibits superior conductivity with a resistivity of 8.28×10^{-5} Ω·cm, high stretchability (250%), and high working stability (small resistance changes during the deformation process) and mechanical durability (bent or twisted 10000 times). The high stability and high stretchability are attributed to the fact that the AgNDs have a treelike structure and with high aspect ratio, which can act as a bridge between the disconnected networks of AgMFs generated by bending, twisting, or stretching. The AgMFs/AgNDs/TPU flexible conductive composites demonstrate superior electromechanical performances as flexible and stretchable conductors, which may be useful for wearable and stretchable electronics applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b01943.

Figures S1−S7 (PDF)

Video S1: tensile movie of AgMFs/AgNDs/TPU flexible electrical conductive films (AVI)

Video S2: LED luminance change movie during the stretching process of AgMFs/AgNDs/TPU flexible electrical conductive films (AVI)

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The authors declare no competing financial interest.

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REFERENCES

(1) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C.-K.; Hellstrom, S. L.; Lee, J. A.; Fox, C. H.; Bao, Z. Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes. *Nat. Nanotechnol.* **2011**, *6* (12), 788−792.

(2) Wang, X.; Gu, Y.; Xiong, Z.; Cui, Z.; Zhang, T. Silk-molded flexible, ultrasensitive, and highly stable electronic skin for monitoring human physiological signals. *Adv. Mater.* **2014**, *26* (9), 1336−1342.

(3) Wang, S.; Oh, J. Y.; Xu, J.; Tran, H.; Bao, Z. Skin-Inspired Electronics: An Emerging Paradigm. *Acc. Chem. Res.* **2018**, *51*, 1033−1045.

(4) Hanif, A.; Trung, T. Q.; Siddiqui, S.; Toi, P. T.; Lee, N. E. Stretchable, Transparent, Tough, Ultrathin and Self-limiting Skin-like Substrate for Stretchable Electronics. *ACS Appl. Mater. Interfaces* **2018**, *10* (32), 27297−27307.

(5) Russo, A.; Ahn, B. Y.; Adams, J. J.; Duoss, E. B.; Bernhard, J. T.; Lewis, J. A. Pen-on-paper flexible electronics. *Adv. Mater.* **2011**, *23* (30), 3426−3430.

(6) Yang, C.; Lin, W.; Li, Z.; Zhang, R.; Wen, H.; Gao, B.; Chen, G.; Gao, P.; Yuen, M. M. F.; Wong, C. P. Water-Based Isotropically Conductive Adhesives: Towards Green and Low-Cost Flexible Electronics. *Adv. Funct. Mater.* **2011**, *21* (23), 4582−4588.

(7) Moon, H. C.; Lodge, T. P.; Frisbie, C. D. Solution-Processable Electrochemiluminescent Ion Gels for Flexible, Low-Voltage, Emissive Displays on Plastic. *J. Am. Chem. Soc.* **2014**, *136* (9), 3705−3712.

(8) White, M. S.; Kaltenbrunner, M.; Głowacki, E. D.; Gutnichenko, K.; Kettlgruber, G.; Graz, I.; Aazou, S.; Ulbricht, C.; Egbe, D. A. M.; Miron, M. C. Ultrathin, highly flexible and stretchable PLEDs. *Nat. Photonics* **2013**, *7* (10), 811−816.

DOI: 10.1021/acsanm.8b01943
ACS Appl. Nano Mater. 2019, 2, 351−359

(9) Lu, X.; Yu, M.; Wang, G.; Tong, Y.; Li, Y. Flexible solid-state supercapacitors: design, fabrication and applications. *Energy Environ. Sci.* **2014**, *7* (7), 2160−2181.
(10) Ren, J.; Ren, R. P.; Lv, Y. K. Stretchable all-solid-state supercapacitors based on highly conductive polypyrrole-coated graphene foam. *Chem. Eng. J.* **2018**, *349*, 111−118.
(11) Yao, S.; Zhu, Y. Wearable multifunctional sensors using printed stretchable conductors made of silver nanowires. *Nanoscale* **2014**, *6* (4), 2345−2352.
(12) Lee, J. H.; Yang, D.; Kim, S.; Park, I. Stretchable strain sensor based on metal nanoparticle thin film for human motion detection & flexible pressure sensing devices. *Nanoscale* **2014**, *6* (20), 11932−11939.
(13) Liang, B.; Lin, Z.; Chen, W.; He, Z.; Zhong, J.; Zhu, H.; Tang, Z.; Gui, X. Ultra-stretchable and highly sensitive strain sensor based on gradient structure carbon nanotubes. *Nanoscale* **2018**, *10*, 13599−13606.
(14) Wang, X.; Li, J.; Song, H.; Huang, H.; Gou, J. Highly Stretchable and Wearable Strain Sensor Based on Printable Carbon Nanotube Layers/Polydimethylsiloxane Composites with Adjustable Sensitivity. *ACS Appl. Mater. Interfaces* **2018**, *10* (8), 7371−7380.
(15) Lee, S.; Shin, S.; Lee, S.; Seo, J.; Lee, J.; Son, S.; Cho, H. J.; Algadi, H.; Al - Sayari, S.; Kim, D. E.; Lee, T. Ag Nanowire Reinforced Highly Stretchable Conductive Fibers for Wearable Electronics. *Adv. Funct. Mater.* **2015**, *25* (21), 3114−3121.
(16) Han, J. T.; Bo, H. J.; Seo, S. H.; Roh, K. C.; Kim, S.; Choi, S.; Woo, J. S.; Kim, H. Y.; Jang, J. I.; Shin, D. C. Dispersant-free conducting pastes for flexible and printed nanocarbon electrodes. *Nat. Commun.* **2013**, *4* (1), 1−8.
(17) Rogers, J. A.; Someya, T.; Huang, Y. Materials and Mechanics for Stretchable Electronics. *Science* **2010**, *327* (5973), 1603−1607.
(18) Sekitani, T.; Noguchi, Y.; Hata, K.; Fukushima, T.; Aida, T.; Someya, T. A rubberlike stretchable active matrix using elastic conductors. *Science* **2008**, *321* (5895), 1468−1472.
(19) Lacour, S. P.; Wagner, S.; Huang, Z.; Suo, Z. Stretchable gold conductors on elastomeric substrates. *Appl. Phys. Lett.* **2003**, *82* (15), 2404−2406.
(20) Khang, D. Y.; Xiao, J.; Kocabas, C.; Maclaren, S.; Banks, T.; Jiang, H.; Huang, Y. Y.; Rogers, J. A. Molecular scale buckling mechanics in individual aligned single-wall carbon nanotubes on elastomeric substrates. *Nano Lett.* **2008**, *8* (1), 124−30.
(21) Ahn, B. Y.; Lewis, J. A. Omnidirectional Printing of Flexible, Stretchable, and Spanning Silver Microelectrodes. *Science* **2009**, *323* (5921), 1590−1593.
(22) Ahn, J. H.; Je, J. H. Stretchable electronics: materials, architectures and integrations. *J. Phys. D: Appl. Phys.* **2012**, *45* (10), 103001.
(23) Chen, M.; Tao, T.; Zhang, L.; Gao, W.; Li, C. Highly conductive and stretchable polymer composites based on graphene/MWCNT network. *Chem. Commun.* **2013**, *49* (16), 1612−1614.
(24) Zhu, Y.; Xu, F. Buckling of Aligned Carbon Nanotubes as Stretchable Conductors: A New Manufacturing Strategy. *Adv. Mater.* **2012**, *24* (8), 1073−1077.
(25) Zhang, Y.; Sheehan, C. J.; Zhai, J.; Zou, G.; Luo, H.; Xiong, J.; Zhu, Y. T.; Jia, Q. X. Polymer-embedded carbon nanotube ribbons for stretchable conductors. *Adv. Mater.* **2010**, *22* (28), 3027−3031.
(26) Wu, H.; Hu, L.; Rowell, M. W.; Kong, D.; Cha, J. J.; Mcdonough, J. R.; Zhu, J.; Yang, Y.; Mcgehee, M. D.; Cui, Y. Electrospun Metal Nanofiber Webs as High-Performance Transparent Electrode. *Nano Lett.* **2010**, *10* (10), 4242−4248.
(27) Harris, J.; Graudejus, O.; Wagner, S. Elastically Stretchable Insulation and Bilevel Metallization and Its Application in a Stretchable RLC Circuit. *J. Electron. Mater.* **2011**, *40* (6), 1335−1344.
(28) Zhao, S.; Li, J.; Cao, D.; Gao, Y.; Huang, W.; Zhang, G.; Sun, R.; Wong, C. P. Percolation threshold-inspired design of hierarchical multiscale hybrid architectures based on carbon nanotubes and silver nanoparticles for stretchable and printable electronics. *J. Mater. Chem. C* **2016**, *4* (27), 6666−6674.
(29) Li, W.; Li, F.; Li, H.; Su, M.; Gao, M.; Li, Y.; Su, D.; Zhang, X.; Song, Y. Flexible Circuits and Soft Actuators by Printing Assembly of Graphene. *ACS Appl. Mater. Interfaces* **2016**, *8* (19), 12369−12376.
(30) Lee, C.; Oh, Y.; Yoon, I. S.; Kim, S. H.; Ju, B. K.; Hong, J. M. Flash-induced nanowelding of silver nanowire networks for transparent stretchable electrochromic devices. *Sci. Rep.* **2018**, *8* (1), 1−10.
(31) Rangari, V. K.; Yousuf, M.; Jeelani, S.; Pulikkathara, M. X.; Khabashesku, V. N. Alignment of carbon nanotubes and reinforcing effects in nylon-6 polymer composite fibers. *Nanotechnology* **2008**, *19* (24), 245703.
(32) Oh, J. Y.; Lee, D.; Hong, S. H. Ice-Templated Bimodal-Porous Silver Nanowire/PDMS Nanocomposites for Stretchable Conductor. *ACS Appl. Mater. Interfaces* **2018**, *10*, 21666−21671.
(33) Wei, Y.; Chen, S.; Li, F.; Liu, K.; Liu, L. Hybrids of Silver Nanowires and Silica Nanoparticles as Morphology Controlled Conductive Filler Applied in Flexible Conductive Nanocomposites. *Composites, Part A* **2015**, *73*, 195−203.
(34) Lee, S. J.; Kim, J. W.; Park, J. H.; Porte, Y.; Kim, J. H.; Park, J. W.; Kim, S.; Myoung, J. M. SWCNT−Ag nanowire composite for transparent stretchable film heater with enhanced electrical stability. *J. Mater. Sci.* **2018**, *53* (17), 12284−12294.
(35) Ma, H.; Li, Z.; Tian, X.; Yan, S.; Li, Z.; Guo, X.; Ma, Y.; Ma, L. Silver Flakes and Silver Dendrites for Hybrid Electrically Conductive Adhesives with Enhanced Conductivity. *J. Electron. Mater.* **2018**, *47* (5), 1−11.
(36) Wen, X.; Xie, Y. T.; Mak, M. W. C.; Cheung, K. Y.; Li, X. Y.; Renneberg, R.; Yang, S. Dendritic Nanostructures of Silver: Facile Synthesis, Structural Characterizations, and Sensing Applications. *Langmuir* **2006**, *22* (10), 4836−4842.
(37) Fang, J.; You, H.; Kong, P.; Yi, Y.; Song, X.; Ding, B. Dendritic Silver Nanostructure Growth and Evolution in Replacement Reaction. *Cryst. Growth Des.* **2007**, *7* (5), 864−867.
(38) Sun, M.; Qian, H.; Liu, J.; Li, Y.; Pang, S.; Xu, M.; Zhang, J. A flexible conductive film prepared by the oriented stacking of Ag and Au/Ag alloy nanoplates and its chemically roughened surface for explosive SERS detection and cell adhesion. *RSC Adv.* **2017**, *7* (12), 7073−7078.
(39) Yang, C.; Cui, X.; Zhang, Z.; Chiang, S. W.; Lin, W.; Duan, H.; Li, J.; Kang, F.; Wong, C. P. Fractal dendrite-based electrically conductive composites for laser-scribed flexible circuits. *Nat. Commun.* **2015**, *6* (1), 1−10.
(40) Qiang, Y. X.; Zhu, C. H.; Liu, Y.; Cui, S. Fabrication of highly conductive silver nanowires flexible conductor based on polydopamine-modified goose down network. *J. Mater. Sci.: Mater. Electron.* **2018**, *29* (8), 6388−6396.
(41) Zhang, S.; Li, Y.; Tian, Q.; Liu, L.; Yao, W.; Chi, C.; Zeng, P.; Zhang, N.; Wu, W. Highly conductive, flexible and stretchable conductors based on fractal silver nanostructures. *J. Mater. Chem. C* **2018**, *6* (15), 3999−4006.
(42) Bhanushali, S.; Ghosh, P.; Ganesh, A.; Cheng, W. 1D copper nanostructures: progress, challenges and opportunities. *Small* **2015**, *11* (11), 1232−1252.
(43) Liu, K.; Sun, Y.; Lin, X.; Zhou, R.; Wang, J.; Fan, S.; Jiang, K. Scratch-resistant, highly conductive, and high-strength carbon nanotube-based composite yarns. *ACS Nano* **2010**, *4* (10), 5827−5834.
(44) Ajmal, C. M.; Menamparambath, M. M.; Choi, H. R.; Baik, S. Extraordinarily high conductivity of flexible adhesive films by hybrids of silver nanoparticle-nanowires. *Nanotechnology* **2016**, *27* (22), 225603.
(45) Ma, R.; Kwon, S.; Zheng, Q.; Kwon, H. Y.; Kim, J. I.; Choi, H. R.; Baik, S. Carbon-Nanotube/Silver Networks in Nitrile Butadiene Rubber for Highly Conductive Flexible Adhesives. *Adv. Mater.* **2012**, *24* (25), 3344−3349.
(46) Lu, Y.; Jiang, J.; Yoon, S.; Kim, K. S.; Kim, J. H.; Park, S.; Kim, S. H.; Piao, L. High-Performance Stretchable Conductive Composite Fibers from Surface-Modified Silver Nanowires and Thermoplastic Polyurethane by Wet Spinning. *ACS Appl. Mater. Interfaces* **2018**, *10* (2), 2093−2104.

DOI: 10.1021/acsanm.8b01943
ACS Appl. Nano Mater. 2019, 2, 351−359

(47) Li, L. M.; Zhu, C. H.; Wu, Y. P.; Wang, J. H.; Zhang, T. L.; Liu, Y. A conductive ternary network of a highly stretchable AgNWs/AgNPs conductor based on a polydopamine-modified polyurethane sponge. *RSC Adv.* **2015**, *5* (77), 62905−62912.
(48) Huang, W.; Li, J.; Zhao, S.; Han, F.; Zhang, G.; Sun, R.; Wong, C. P. Highly electrically conductive and stretchable copper nanowires-based composite for flexible and printable electronics. *Compos. Sci. Technol.* **2017**, *146* (7), 169−176.

DOI: 10.1021/acsanm.8b01943
ACS Appl. Nano Mater. 2019, 2, 351−359