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Aligned Silver Nanowires Enabled Highly Stretchable and Transparent Electrodes with Unusual Conductive Property

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Transparent conductors (TCs) for the next generation of soft electronic devices need to be highly stretchable, conductive and transparent; while inevitable challenge lies in enhancing them simultaneously. Cost effective silver nanowires (AgNWs) were widely used but the conventional random network gives high junction resistance as well as the degraded conductivity at stretched state. Here a novel, facile and versatile agitation-assisted assembly approach is reported to control the orientation direction and density of AgNWs and to Layer-by-Layer deposit the AgNWs monolayer or multilayers onto the pre-strained soft substrate. Such electrode gives the unprecedented low sheet resistance of $2.8 \Omega \text{ sq}^{-1}$ as well as high transparency of 85% and high stretchability of 40%. It is interesting to note that contrary to most other reports, such device shows higher conductivity at the stretched state compared to the released state.

1. Introduction

In recent decades, many attentions have been paid to stretchable and transparent electrodes due to the emergence of next-generation devices having irregular shapes on nonrigid and nonplanar substrates. The commonly used conductive materials are conductive transparent ceramic including indium tin oxide (ITO),^[1-4] fluorine doped Tin Oxide (FTO),^[5] and aluminum doped zinc oxide (ATO),^[6] which are severely limited by their intrinsic fracture characteristic, lack of resources and harsh processing conditions. As such, a variety of conductive films with mechanical stretchability and optical transparency, such as metal nanowires,^[7-14] alloyed metal nanowires,^[15] carbon nanotubes,^[16-18] graphene,^[19, 20] conducting polymers^[21] and hybrids of metal nanowires and graphene^[22] have been fabricated. Among these stretchable transparent conductive materials, metal nanowires based electrodes are intensively investigated because of the easy fabrication process and excellent electrical conductivity. However, the random metal nanowire nanostructures in these electrodes can give high junction resistance, electrical short-circuits and leakages, degraded conductivity at the stretched state, which hinder the performance of the electrodes.^[23] Therefore, we for the first time proposed a facile approach to Layer-by-Layer deposit the AgNWs onto prestrained flexible substrates with well controlled orientation

Currently, various assembly strategies have been developed to align the one-dimensional nanostructures in ordered way. Some strategies such as rubbing,^[24] external field assisted assembly,^[25-28] coassembly,^[29] bubble-blowing,^[30] dip-coating,^[31] printing,^[32, 33] chemical bonding,^[34] strain-release assembly,^[35] wrinkle-assisted assembly,^[36] shear-coating^[37, 38] and interface-mediated assembly^[39-41] can lead to a single oriented layer. And some strategies including Langmuir-Blodgett technique,^[42, 43] evaporation induced assembly,^[44] electrospinning,^[45, 46] fluidic flow,^[47] spray coating^[48, 49] and brush coating^[50, 51] can be repeated to form multilayered oriented structures. However, there are still some inherent limitations that

severely restrict their applications as some of the above techniques require complicated process or specialized equipment such as additional transfer process, surface patterning, spraying nozzles and special substrates, which limit the cost-effective assembly of high density nanowires in a controlled manner.

Herein, a simple method for alignment of AgNWs was introduced by using a Layer-by-Layer agitation-assisted alignment technique for the fabrication of highly stretchable and transparent electrode. One of the advantages is that by simply controlling the agitation speed, duration and the viscosity of the solvent, the well aligned nanowire can be assembled layer by layer. Compared to other reports, our approach gives the advantages of facile fabrication set up, large-area ordered nanostructures, no constrain on substrates, multilayered aligned structures and unprecedented combination of high conductivity, high stretchability and high transparency.^[9, 11-13, 15-20, 52] Alignment of AgNWs into mesh-like structures to improve the conductivity and transparency have been recently reported,^[53, 54] but their assembly techniques are much more complicated than the strategy we propose here. Meanwhile these electrodes were prepared on unstretched substrates thus they would decrease performances at the stretched state. It is interesting to note that our stretchable electrodes give higher conductivity at the stretched state compared to the released one, which is opposite to the previous reports. This facile approach provides a new way to assemble one-dimensional nanostructures into well controlled monolayer or multilayer architectures on various substrates. The highly stretchable and transparent electrodes fabricated from the oriented AgNWs show promising applications in the field of high-performance electronic and optoelectronic nano devices.

2. Results and Discussion

The new agitation assisted approach works with simple set up of mixing AgNWs suspension

into well controlled viscous solvent. The starting individual silver nanowire (Zeta potential: -33 mV) has the diameter of 40-60 nm and the aspect ratio of ~ 120 (Figure S1, Supporting Information). By simply controlling the agitation speed and duration, a monolayer of AgNWs can be aligned well onto the prestrained Poly(ethyleneimine) (PEI) coated polydimethylsiloxane (PDMS) substrates (**Figure 1a** left). The digital image of the experimental set up is shown in Figure S2a (Supporting Information). The PEI used is a polycation, it possesses positive charges in aqueous solution, therefore it can be employed as a binder of two negatively charged UV ozone treated substrate and AgNWs. Moreover, it can preserve the orientation of AgNWs underlayers while coating new layer of AgNWs. Furthermore, the SEM image (Figure 1b) and the anisotropic sheet resistance (Figure 1b insert) confirm the well oriented characteristic. It can be observed that the majority of the AgNWs are oriented along the same orientation as the liquid flowing direction, due to the shear force induced by the liquid flow with only a small number of deviations can be observed. The sheet resistances measured from alignment direction and the orthogonal direction give distinct value of 12 and $49 \Omega \text{ sq}^{-1}$ respectively. The conductivity in aligned direction is higher than that in the orthogonal direction as there are more pathways for conducting the electrons.

By simply rotating the prestrained PDMS substrate and repeating the assembly process, a “mesh-like” nanostructure was fabricated (Figure 1a middle) which is consistent with the SEM observations at the 40% stretched state (Figure 1c). The SEM image shows a clearly crossed aligned mesh-like structure since the orientation of AgNWs was achieved when the PDMS substrate was prestrained. A released mesh gives the final product as illustrated in Figure 1a (right) and the SEM (Figure 1d) as it can be seen that the AgNWs are more tangled at the released state while still maintains the contact between the two-layered AgNWs to form conductive paths on the released PDMS substrates. The digital image of a sample is shown in Figure S2b (Supporting Information). Moreover, more complicated multilayered structures can

be prepared with the Layer-by-Layer agitation-assisted alignment by changing the position and direction of the PDMS substrate, Figure S3 (Supporting Information) presents a three-layered oriented AgNWs-based nanostructure with different orientation in each layer. By using this simple Layer-by-Layer alignment, a highly stretchable transparent electrode with ultra low sheet resistance, high optical transparency and high stretchability can be successfully obtained simultaneously.

It was found that the agitation speed is one of the factor to influence the alignment of AgNWs. **Figure 2a, b, c** show the SEM images of the AgNWs oriented at 200, 500 and 800 rpm respectively. There is no preferential alignment of the AgNWs in 200 rpm sample and the density of the AgNWs coated on the PDMS substrate is low (Figure 2a), which may due to the weak shear force at this agitation speed. When the agitation speed is increased to 500 rpm and 800 rpm, both samples could be aligned well along the liquid flowing direction. The SEM images were then analyzed with the plugin orientation J^[55] developed for Image J,^[56] and the distribution of the angle θ between the principal axis of each nanowire and the liquid flowing (agitation) direction was extracted (Figure 2d, e and f). The sample with 200 rpm agitated speed does not show any ordered orientation. In contrast, the samples agitated at both 500 and 800 rpm have good ordered orientation, which exhibit the predominant red color. The 2D order parameter (S_{2D}) is calculated and be used to characterize the degree of orientation.

$$S_{2D} = \langle 2 \cos^2 \theta - 1 \rangle \quad (1)$$

The S_{2D} shows values between 0 and 1, where $S_{2D} = 0$ corresponds to a random distribution of AgNWs (isotropic films) and $S_{2D} = 1$ corresponds to a perfectly parallel alignment (anisotropic films). For the AgNWs prepared at 200 rpm, a low S_{2D} (0.28) was observed with nearly even orientation distribution along all the directions (Figure 2g). On the other hand, the distribution of orientation of the AgNWs oriented at 500 rpm and 800 rpm show high and comparable S_{2D} (0.80 and 0.82 for 500 rpm and 800 rpm, respectively) which correspond to a narrow

distribution in the orientation chart (Figure 2h and 2i). It suggests that $\sim 90\%$ of the AgNWs in the 500 rpm and 800 rpm samples are aligned within $\pm 30^\circ$, and $\sim 50\%$ of the AgNWs within $\pm 10^\circ$. Figure 2j summarize the relationship between S_{2D} and the agitation speed and it shows that S_{2D} increases with increasing speed up to 500 rpm and remains constant after 500 rpm. When the agitation speed is higher than 600 rpm, splashing of the AgNWs suspension happens, thus 500 rpm is the best agitation speed for orientation of the AgNWs.

Similarly, the effect of viscosity of the solvent were studied systematically by changing the percentage of ethylene glycol in water. Figure S4 (Supporting Information) shows the SEM images of the AgNWs oriented at the speed of 500 rpm in different ethylene glycol containing water (Figure S4a: 0%, v/v; Figure S4b: 50%, v/v; Figure S4c: 100%, v/v). It can be seen that the most AgNWs show a disordered orientation in pure water (0%, v/v) due to the low viscosity of the water, which corresponds to the low S_{2D} (0.41) (Figure S4a, d, g). When the percent of ethylene glycol in water is 50%, the S_{2D} reached to a maximum value of 0.80 (Figure S4b, e, h). Figure S4c shows the AgNWs oriented in ethylene glycol (100%, v/v), the AgNWs were coated on PDMS substrate for 48 hours. It was found that the coverage of the AgNWs coated on the PEI-coated PDMS substrate is low, which may be due to the poor solubility of PEI in ethylene glycol. The S_{2D} of AgNWs in pure ethylene glycol is about 0.60 (Figure S4f, i). The influence of the percentage of ethylene glycol in water on the order parameter is shown in Figure 2k. It can be seen that the S_{2D} reaches a peak (~ 0.80) for the ethylene glycol concentration of 50%, which agrees with the analysis above. Therefore, the optimum percentage of ethylene glycol in water for the orientation and coverage of AgNWs is 50%. This assembly technique can be applied on other types of substrate, Figure S5 (Supporting Information) shows the SEM images of the AgNWs oriented on glass slide (Figure S5a) and silicon wafer (Figure S5b) in ethylene glycol containing water (50%, v/v) at the agitation speed of 500 rpm.

The strain-dependent optical transmittances of the AgNWs electrodes of different coating durations are demonstrated in **Figure 3a** (10 mins) and Figure S6 (30 and 60 mins, Supporting Information), the AgNW density were $24 \mu\text{g cm}^{-2}$, $31 \mu\text{g cm}^{-2}$ and $33 \mu\text{g cm}^{-2}$ for 10 mins sample, 30 mins sample and 60 mins sample, respectively. The UV-vis of the AgNWs suspension has the two absorption peaks at 349 nm and 377 nm (Figure S7, Supporting Information). It was found that the optical transmittances increased for $\sim 15\%$ as the applied strain was increased from 0% to 40%. The photographs of the as-prepared AgNWs-based electrode at the different stretched states are shown in Figure 3b. All the samples show high transparency. Figure 3c presents the transmittances at 550 nm of the oriented AgNWs based electrodes with different coating time in each layer. For both the stretched and the released state, the transmittances decline with the increasing of the coating time, the transmittances at 550 nm at the released state are 71.8%, 65.2% and 63.9% for 10, 30 and 60 mins sample respectively, these values can increase to 85.2%, 77.1%, 75% when the samples were stretched for 40%. This observation can be explained by the relationship between the AgNWs density and the coating time. The density of the AgNWs increases with increasing of the coating time (Figure S8, Supporting Information). Therefore, the optical transparency is controllable via adjusting the silver nanowire density by varying coating time.

Interestingly, it can also be found from Figure 3c that there is no significant difference in transmittance for the 30 mins sample and 60 mins sample, this phenomenon may because the AgNWs are only able to adsorb onto regions where a PEI-coated interface is available, but are unable to coat directly on the layer of AgNWs since the weak interactions exist among AgNWs. These are the main reasons why monolayered AgNWs can be obtained. As more and more nanowires are deposited, the “free places” for new nanowires to interact with the PDMS substrate is limited, and the deposition rate reduces accordingly. As a result the surface coverage reaches a plateau for longer coating times and this result is consistent with the other reports.^[49]

The conductivity of various density AgNWs network at different strain is demonstrated in Figure 3d. The sheet resistance of the obtained AgNWs network assembled with AgNWs for 10 mins in each layer is $13 \Omega \text{ sq}^{-1}$ at the released state. While the coating time in each layer is increased to 60 mins, the sheet resistance of the obtained electrode decreases to $4.4 \Omega \text{ sq}^{-1}$. Therefore, the sheet resistance decreases with the increasing coating time of AgNWs. On the other hand, the sheet resistance decreases with the applied strain. When the sample assembled with AgNWs for 10 mins in each layer is stretched for 40%, the sheet resistance is lowered 4.5 times compared to the released state (Stretched state: $\sim 2.8 \Omega \text{ sq}^{-1}$; release state: $13 \Omega \text{ sq}^{-1}$). This result is opposite to the results reported in the literatures (Figure 3e).^[12, 13, 57] The two cases reported by literatures showed higher or similar sheet resistance at the initial state, but it increased dramatically through the stretching process because of the randomly oriented AgNWs structures. The sheet resistance increased about 7 times and 2 times for the samples from ref. 12 and ref. 57, respectively, and the sheet resistance can be up to $100 \Omega \text{ sq}^{-1}$ at the stretched state. In contrast, the aligned AgNWs samples reported in this work show lower sheet resistance at the stretched state, which may be due to the fact the AgNWs were oriented on a prestrained PDMS substrate. While the AgNWs electrodes are stretched, the nanostructures of the coated AgNWs change from the tangled orientation to the oriented “mesh-like” nanostructures, in which there are less junction resistance and electrical short-circuits, with better conductive performance. It is also notable that the decrease in resistance compared to its initial resistance (R/R_0) is suppressed for the electrode with higher AgNWs density. For instance, the 60 mins sample has the sheet resistance of $4.4 \Omega \text{ sq}^{-1}$ at the released state and $1.92 \Omega \text{ sq}^{-1}$ at the stretched state, which may due to an increase in fused interconnections between AgNWs.^[12] Indeed, the electrode with unstretched PDMS under the same assembly condition was prepared as a comparison. The electrode exhibits similar low resistance at the released state ($2.5 \Omega \text{ sq}^{-1}$), but with even 10% strain, the resistance increased dramatically to $30 \text{ k}\Omega \text{ sq}^{-1}$. The phenomenon may be due to the inner nanostructure was destroyed under stress (Figure S9, Supporting

Information). The changes of AgNWs orientation at each stretch state is shown in Figure S10 (Supporting Information). Figure S10 (a-e) and Figure S10 (f-i) demonstrate the SEM images and the orientation maps of the 60 mins sample stretched for 0%, 10%, 20%, 30% and 40% respectively. It is observed that the AgNWs changed from a tangled orientation (0% strain) into crossed “mesh-like” orientation (40% strain).

To evaluate the optical and conductive performances of our electrodes, the transmittance and sheet resistance were compared by simulation. Figure 3f insert shows the models of the random network and the mesh-like network. The simulation shows that mesh-like structure has a higher transmittance than the random network (Figure 3f), which is consistent with experimental results (Figure 3f), therefore the transparency can be enhanced by aligning the nanowires. The discrepancy between the experimental and simulation values are mainly due to the fact that the simulation assumes the perfect alignment with order parameter of 1 while the highest order parameter can be achieved in experiment is only 0.8. The simulated sheet resistance is $2.15 \Omega \text{ sq}^{-1}$ for “mesh-like” structure (Figure S11), which is consistent with the experimental results (Figure 3d)

These AgNWs based electrodes also show excellent mechanical durability. A 30 mins sample was repeatedly released and 40% stretched for 100 cycles and the conductivity for both states were recorded (Figure 3g). It can be seen that after cycling, the conductivity of this electrode remains almost the same at the released state, giving a value of $\sim 6.2 \Omega \text{ sq}^{-1}$; and the sheet resistance at the stretched state increases slightly.

The Joule heating properties of the oriented AgNWs based electrode were also studied. **Figure 4a** presents the time dependent temperatures at various applied voltage, while the voltage is increased by 1 V every 20 seconds until the heater fails at 10 V bias voltage. The average temperature increases proportionally to the square of applied voltage. Figure 4b present the heating behavior of the electrode from 1 to 9 V. It shows that the temperature of the electrode

increased rapidly and reaches a steady-state temperature within 60 seconds. When the power is cut off, the temperature drops back to room temperature again at the same rate. As the steady-state temperature of device can be increased from 28.5 °C to 74.6 °C with applied voltage increasing from 1 to 9 V, it can be concluded that the temperature of the device can be controlled by varying the input voltage.

The electrothermal performance of the electrode was further tested by applying a stepwise increased voltage at different strains (Figure 4c). The device exhibited rapid response in temperature upon the application of voltage, the steady-state temperatures for the device after 3 mins are 40, 44.4, 49.4 and 55.8 °C for 0%, 10%, 20% and 30% strain, respectively. The observation indicates that the resistance is reduced when a strain is applied, since the heat produced by Joule heating at a fixed bias voltage is inversely proportional to the resistance of the target electrode,^[12] which is consistent with Figure 3e. The durability of voltage dependent Joule heating is also tested in both 0% or 30% strained sample under 4 V and 6 V voltage (Figure 4d). After 6 test cycles, the reversibility electrothermal performance for both stretched and unstretched sample remains the same, which indicates that these electrodes have good durability for generating the Joule heating.

The optical, mechanical and electrical properties of designed oriented AgNW/PDMS composite electrodes have been compared with previously reported stretchable transparent electrodes. As shown in **Figure 5a**, the designed oriented AgNWs based electrode exhibits a significantly lower sheet resistance, higher or comparable transparency and stretchability than other reported electrodes, including AgNWs,^[9, 11-14, 58-61] AgNWs@Graphene,^[62] Ag mesh,^[63] Ag nanofiber,^[64] Au-Ag core-shell nanowires,^[15] CuNWs,^[65, 66] Cu@Cu₄Ni,^[52] CNT,^[16, 17] CNT mesh,^[18] CNT embroidered graphene,^[67] graphene,^[19, 20, 68] Au nanotrough,^[69] Au nanomesh^[70] and CuZr nanotrough.^[71] Our AgNWs based electrodes possess this superior optical and electrical property may because the AgNWs were crosswise aligned into a “mesh-like” structure

through the Layer-by-Layer alignment. The crossed aligned “mesh-like” AgNW structure can achieve a balance between the optical transmittance and the electrical conductivity, since it can reduce the nanowire density significantly and lower the electrical percolation threshold compared to the random oriented AgNWs networking.^[72, 73] Our oriented AgNWs based electrode can illuminate an LED lamp biased at 3V with 0% strain (Figure 5b left), with 40% strain (Figure 5b right) and bended with $\sim 180^\circ$ (Figure 5c). From these results we can conclude that our oriented AgNWs based electrode can simultaneously achieve low sheet resistance, high optical transparency and remarkable stretchability, and is suitable as electrodes for stretchable and flexible transparent electronic devices.

3. Conclusion

In this work, a facile and versatile approach for fabricating oriented AgNWs was demonstrated for the first time. The alignment mainly depends on the viscosity of the solvents, rotating speeds and the coating time. Moreover, multilayered architecture can be fabricated readily by simply repeating the same procedure on designated oriented substrates. Such approach has been successfully demonstrated to fabricate a highly stretchable electrode with record high conductivity $2.8 \Omega \text{ sq}^{-1}$ at the transparency of 85% and high stretchability of 40%. Moreover, the electrodes showed a unique positive relationship between the conductivity and strain, which is different from the previous reported cases due to the much ordered and aligned nanostructures at the stretched state and this was further confirmed by Joule heating demonstrations. This highly cost effective and facile assembly strategy to align monolayer and multilayer of one-dimensional materials may open new avenue for precisely controlling the nanostructures in many different applications.

4. Experimental Section

Materials: Poly(ethyleneimine) (PEI, $M_n \approx 60,000$ g/mol), Polyvinylpyrrolidone (PVP, $M_w \approx 40,000$), Silver nitrate, Sodium chloride, Ethylene glycol and Glycerol were purchased from Sigma-Aldrich. All the chemicals were used without further purification. The aqueous solutions were prepared with ultrapure water (resistivity = $18.2 \text{ M}\Omega\cdot\text{cm}$, Milli Q-Gradient system).

Synthesis of AgNWs: Uniform Ag nanowires were prepared according to literature.^[74] 1.76 g of PVP ($M_w \approx 40,000$) was added into 57 mL of glycerol and the solution was kept at 100°C under stirring for 2 hours to form a homogeneous solution. After cooling down to room temperature, 0.474 g of AgNO_3 was added into the solution. Then a NaCl solution (17.7 mg of NaCl dissolving in 0.15 mL of ultrapure water and 3 mL of glycerol) was added. The solution was heated from room temperature to 210°C in 30 minutes under agitation. When temperature reached 210°C , the heating was stopped and the mixture was cooled down to 100°C . 60 mL of ultrapure water was added, and then the temperature returned to room temperature. The solution was kept undisturbed for 1 week and the sediment at the bottom of the flask was collected carefully. The obtained Ag nanowires were washed thoroughly with water by centrifuging at 2000 rpm for 30 min.

Orientation of monolayered AgNWs on PDMS substrate: A PDMS substrate was prepared by mixing PDMS solution and curing agent at 10:1 ratio, followed by curing at 60°C for 3 h. Then 100 mL mixture of AgNWs suspended in ethylene glycol-containing water (0.3 mg/mL) was set in a 200 mL beaker and a cylinder-shaped holder (3 cm in diameter and 1.6 cm in height) was placed at the center of the beaker. A magnetic stirring bar (2.8 cm in length) was placed on the holder for the agitation.

PDMS substrates ($1.5 \text{ cm} \times 1.5 \text{ cm}$) were activated by UV ozone for 15 mins, then dipped in PEI aqueous solution (2.5 mg/mL) for 20 mins and rinsed in pure water (3×3 mins). And the PEI-coated PDMS substrates were immersed about 3 cm away from the center of the beaker and parallel to the flowing direction.

For studying the influence of agitation speed on the orientation of AgNWs, the PEI-coated PDMS substrates were immersed in ethylene glycol-containing water (50%, v/v), AgNWs were oriented on them under different agitation speed. After immersion for 30 mins, the substrates were washed with water under the same conditions for 5 mins and dried with N₂ flow.

For studying the influence of percentage of ethylene glycol in water on the orientation of AgNWs, the PEI-coated PDMS substrates were immersed in different percentage of ethylene glycol-containing water, and AgNWs were oriented on them at the agitation speed of 500 rpm, then substrates were washed with water under the same conditions for 5 mins and dried with N₂ flow. For the orientation in mixture of water/ethylene glycol, AgNWs were coated for 30 mins. In the case of pure ethylene glycol, AgNWs were coated for 48 hours.

Preparation of highly stretchable electrode: PDMS substrates (1.5 cm × 1.5 cm) was prestrained for 50% and processed for 15 mins by UV ozone, coated with PEI for 20 mins and rinsed with water (3 × 3 mins). And these substrates were coated with AgNWs by agitation-assisted alignment for 10 mins, 30 mins and 60 mins respectively, after coating the first layer of AgNWs, the PDMS substrates were rinsed with the water under the same conditions for 5 mins and dried with N₂ flow. For coating the second layer of AgNWs, these PDMS substrates were released and rotated for 90°, then prestrained for 50% again. After coating second layer of PEI (20 mins) and rinsed with water (3 × 3 mins), the second layer of AgNWs were coated for the same duration as the first layer for each sample, the 2 layered AgNWs coated PDMS substrates were rinsed with water (5 mins) and dried with N₂ flow again. These obtained PEI/AgNW/PEI/AgNW architectures were marked as 10 mins sample, 30 mins sample and 60 mins sample respectively.

Characterization of AgNWs, AgNWs monolayers and AgNWs based electrode: Scanning electron microscopy (SEM) was performed with a JEOL 6700F equipped with a field emission gun operating at an accelerating voltage of 3 kV. The image analysis was performed using

ImageJ.^[56] The orientation was analyzed by OrientationJ,^[55] a plugin developed for ImageJ. UV-Vis spectra were recorded with a Cary5000 spectrophotometer. Sheet resistance was measured with KEITHLEY 224 4-Point Probe. Resistive Joule heating is induced by applying a constant DC voltage at both ends of the AgNW/PDMS electrode and their response was recorded by an infrared camera.

Simulation: The transmittance was simulated for the cross-aligned AgNWs network and random AgNWs network with the same sheet resistance by software “FDTD solutions”. The diameter of the AgNWs and distance between adjacent nanowires were treated as 60 nm and 600 nm respectively. The $2 \times 2 \mu\text{m}$ AgNW network was treated as mesh unit for calculation. Meanwhile, 2.25 times the amount of AgNWs were applied for the random AgNW network to ensure the same sheet resistance. The sheet resistance of mesh-like structure was simulated by software “COMSOL Multiphysics”, the calculating parameters kept the same as the software “FDTD solutions”.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. a) Schematic illustration of the Layer-by-Layer agitation-assisted alignment. The silver nanowire thin films show a crossed aligned nanostructure at the stretched state and a tangled oriented structure at the released state. b) SEM image of the monolayer assembled AgNWs. (Insert: sheet resistance measured from the orientation direction and the orthogonal direction). c) SEM image of the 10 mins sample after second layer of assembly at the stretched state. d) SEM image of the 10 mins sample at the released state.

Figure 2. SEM images (a, b, c) and orientation-color-coded pictures (d, e, f) and angular distribution (g, h, i) of AgNWs thin films oriented at the speeds of 200 rpm (a, d, g), 500 rpm (b, e, h) and 800 rpm (c, f, i). The inset in picture d) corresponds to the color code for orientation. j) Influence of the agitation speed on the order parameter. k) Influence of the percentage of ethylene glycol in water on the order parameter.

Figure 3. a) Transmittances of the 10 mins sample applied with different strain. b) Photographs of the 10 mins sample at different strains (These electrodes were imaged using red flowers as the background). c) Transmittances at 550 nm as function of different coating times. d) Sheet resistance of the samples as function of different strain (dot line: stretching samples; solid line: releasing samples). e) Conductive properties of sample in comparison with the reported result from the literature. f) Simulation and experimental results of the transmittance of the stretchable electrode at different strain. (Insert: Simulation models of the random AgNWs network and mesh-like AgNWs network). g) Sheet resistance of the 30 mins sample at the released state and stretched state as a function of the number of cycles of stretching for 40%.

Figure 4. a) Transient temperature evolution of the electrode under zero strain at stepwise voltage rise from 1 to 10 V. b) Temperature rise profile at different voltage for electrode coated with AgNWs for 30 mins in each layer. c) Transient temperature evolution of the electrode stepwise rise from 2 to 6 V at a constant strain. d) Time dependent temperatures at the surfaces of the AgNWs based electrode.

Figure 5. a) Sheet resistance, stretchability and optical transmittance at 550 nm for oriented AgNWs electrodes with previously reported electrodes including AgNWs,^[9, 11-14, 58-61] AgNWs@Graphene,^[62] Ag mesh,^[63] Ag nanofiber,^[64] Au-Ag core-shell nanowires,^[15] CuNWs,^[65, 66] Cu@Cu₄Ni,^[52] CNT,^[16, 17] CNT mesh,^[18] CNT embroidered graphene,^[67] graphene,^[19, 20, 68] Au nanotrough,^[69] Au nanomesh^[70] and CuZr nanotrough.^[71] for comparison. The designed oriented AgNWs films exhibit relatively lower sheet resistance, higher or comparable transparency and stretchability simultaneously. b) Photograph of the illuminated LED biased at 3 V with our AgNWs based electrode at the released state (left); photograph of the illuminated LED biased at 3 V using our AgNWs based electrode when it was stretched for 40% (right). c) Photograph of the illuminated LED biased at 3 V using our AgNWs based electrode when it was bended for about 180°.

Keyword: transparent electrode, layer-by-layer agitation-assisted alignment, silver nanowires, conductivity, stretchability

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Supporting Information

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Figure S1. SEM images of the obtained silver nanowires. The nanowires have the diameter of 40-60 nm and the aspect ratio of ~ 120 .

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Figure S2. Illustration of agitation-assisted alignment. a) Digital image of the experimental set up; b) Digital image of a cross-aligned AgNW based electrode (The sample was imaged using a red flower as the background).

Figure S3. SEM image of three-layered AgNWs thin film with different orientation in each layer. The orientation direction of the AgNWs in each layer are shown by different arrows. First layer of AgNWs (red color); second layer of AgNWs (yellow color); third layer of AgNWs (blue color).

Figure S4. Orientation of AgNWs in different percent of ethylene glycol-containing water (v/v) at the agitation speed of 500 rpm. SEM images (a, b, c) and orientation-color-coded pictures (d, e, f) and angular distribution (g, h, i) of AgNWs thin films oriented in 0% ethylene glycol containing water for 30 mins (a, d, g), 50% ethylene glycol containing water 30 mins (b, e, h) and 100% ethylene glycol containing water for 48 hours (c, f, i).

Figure S5. Orientation of AgNWs on glass slide and silicon wafer in ethylene glycol-containing water (50%, v/v) at the agitation speed of 500 rpm. SEM images (a, b) and orientation-color-coded pictures (c, d) and angular distribution (e, f) of AgNWs oriented on glass slide (a, c, e) and silicon wafer (b, d, f).

Figure S6. Optical transmittance of the electrode increased with the strain. a) coated with AgNWs for 30 mins in each layer; b) coated with AgNWs for 60 mins in each layer.

Figure S7. UV-vis spectrum of the obtained silver nanowires suspension. The UV-vis spectrum has two peaks at 349 nm and 377 nm.

Figure S8. SEM images of the two layered AgNWs electrodes with different coating time in each layer. a): 30 mins; b) 60 mins.

Figure S9. SEM images of 30 mins sample prepared when the PDMS substrate was unstretched.

a) SEM image of the sample at the released state; b) SEM image of the sample stretched for 40%.

Figure S10. SEM images (a-e) and orientation maps (f-j) of 60 mins sample at different strains.

0% (a, f); 10% (b, g); 20% (c, h); 30% (d, i); 40% (e, j)

Figure S11. Models of the random AgNWs network and cross-aligned AgNWs structure. a) disordered orientation of a released state; b) two layer model of a stretched state.

These two models were set as a $2 \times 2 \mu\text{m}$ unit for calculation. The distance between adjacent nanowires in the cross-aligned AgNWs structure was 600 nm, which was estimated from the SEM images. The diameter and length of the AgNWs were treated as 60 nm and 2000 nm respectively.

We modeled the random AgNWs network by simply breaking the symmetry of cross-aligned AgNWs structure. The number of AgNWs of two structure was kept the same. To compare the difference of their sheet resistance, we used “Electric currents” model of software “COMSOL Multiphysics”. All the AgNWs were oriented on a PDMS substrate, whose electric resistance is very high compared to Ag. One vertical section of the AgNWs unit was connected to the ground and the 1 A current was connected to the opposite section. As a result, the resistance of cross-aligned AgNWs structure was 2.152Ω , and the random one was 3.955Ω . Although the sheet resistance of random AgNWs network could change as we oriented the AgNWs differently, it always tended to be larger than the sheet resistance of cross-aligned structure, which is consistent with the experimental results.