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Ordering Ag nanowire arrays by spontaneous spreading of volatile droplet on solid surface

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Large-area Ag nanowires are ordered by spontaneous spreading of volatile droplet on a wettable solid surface. Compared with other nanowires orientation methods, radial shaped oriented Ag nanowires in a large ring region are obtained in an extremely short time. Furthermore, the radial shaped oriented Ag nanowires are transferred and aligned into one direction. Based on the hydrodynamics, the coactions among the microfluid, gravity effect and the adhesion of substrate on the orientation of the Ag nanowires are clearly revealed. This spreading method opens an efficient way for extreme economic, efficient and “green” way for commercial producing ordered nanowire arrays.

Ag nanowires and other nanowire materials are of great interest for applications due to their important optical and electronic characteristics. However, their disordered arrangement seems to be problematic for use in microelectronics and photonics device fabrication^{1,2}. With alignment, the 1D structure of nanowires enhances their dielectric, electric, and optical properties. 1D structure such as Ag nanowires, carbon nanotubes, large area ordered nanowires or nanorods shaped materials have potential applications in the field effect transistors, which performances depend on degree of nanowire ordering; asymmetric conductive films which often need large area of ordered Ag nanowires (about several centimetres); or Ag nanowires SERs substrates which performances largely depend on the density and the degree of nanowire ordering^{3–5}. In recent years, many techniques have been developed for nanowires alignment, such as Langmuir-Blodgett⁶, fluid flow⁷, suspension evaporation⁸, blown bubble⁹, electro spinning⁹, and mechanical force technique¹⁰. Among these nanowire orientation methods, the evaporation of nanowires suspension is proved to be an economical way for nanowires orientation^{11,12}. By the evaporation induced capillary flow, nanowires can be oriented on a solid surface by drying a drop of solution containing non-volatile solutes^{13,14}. However, there are still limitations in the needs of strict evaporation condition, long time cost (about several hours)¹³ and compatibility of materials.

A similar flow of volatile solutes exists on a solid surface during the spreading process¹⁵. Therefore, the spontaneous spreading of volatile droplet on a wettable solid surface can be considered to align nanowires. Meanwhile, a large uniform film can be easily obtained on a solid or a liquid surface by the spreading of the suspension^{16,17}. However, the alignment of nanowires by spontaneous spreading of droplets on solid surface has been seldom reported.

Results

Herein, we applied the spontaneous spreading of volatile ethanol droplet to align Ag nanowires on solid substrate (e.g. glass and silicon are chose in our experiment). Ag nanowires with average 200 nm in diameter and 30 μm in length used in this study were fabricated according to previous reports^{18,19}, as shown in Fig. 1(b). Considering the dispersion ability of Ag nanowires and the spreading conditions of liquid on solid surface²⁰, Ag nanowires are subsequently suspend in ethanol, as shown in Fig. 1(a). The Ag nanowires ethanol suspension can be considered as a quasi-stable suspension within half an hour. During this time, the dispersion and the mass fraction of Ag nanowires have no obvious changes. Then, the Ag nanowires suspension (about 1wt%) is dropped on silicon surface. In general, we assembled arrays of Ag nanowires through the liquid spreading and evaporation on solid surface, as shown in Fig. 1(c). Similar with the most familiar spreading phenomenon: tears of wine formed on the cup wall²¹, after only about 50 s, a circle shaped Ag nanowires layer is formed on silicon surface by dropping 5 μL of suspension.

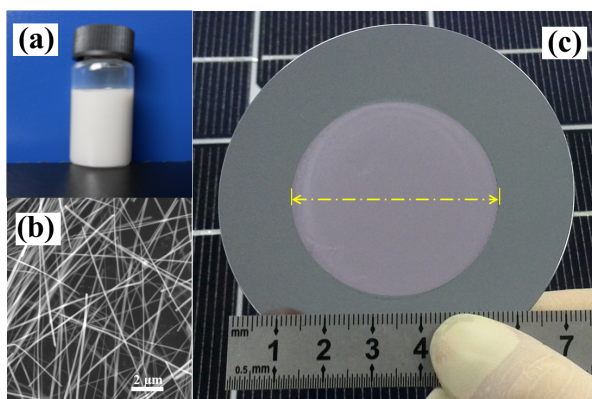


Figure 1 | Suspension of Ag nanowires spreading on silicon surface. (a) Ag nanowire suspension; (b) SEM image of the Ag nanowires; (c) Image of the Ag nanowires array with diameter about 4 cm which is left after the suspension evaporates. The Ag nanowires array is dyed and the diameter is marked by yellow dot line.

A typical example of parallel assembly of Ag nanowires (Fig. 2) shows that virtually all the Ag nanowires are uniformly aligned along the spreading flow direction in a large ring region. As shown in Fig. 2(a), apart from the central region, the scope of ordered Ag nanowires is larger than 2 cm². Due to the preparation technology of Ag nanowires, the lengths of some nanowires are much shorter than others (length range from 5 to 60 μm) (Fig. 2(b) to 2(f)). However, we found that no matter what length of the Ag nanowires, nearly all of these nanowires are aligned along the radius of the circle in the ring region (Fig. 2(b) to 2(f)). In these images, there are some large deviations of Ag nanowires with respect to the flow direction pointed out by yellow dot circles which we will discuss below (Fig. 2(d) and Fig. 2(f)). In order to further study the degree of alignment, we counted the distribution of angles of Ag nanowires in each images and calculated their standard deviation σ , as shown in Table I.

Through the statistics, we found that the average standard deviation of the angles of Ag nanowires is 5.15. Although the density of

Table I | The average angles of Ag nanowires, which is the average angle of the directions of Ag nanowires with that of the vertical direction in each image and the angles standard deviation (the numbers are the image label in Fig. 2.)

	Numbers of Ag nanowires	Average angles (degree)	σ (degree)
(d)	117	72.98	6.63
(e)	64	68.27	5.00
(f)	120	23.99	3.83
Average	—	—	5.15

ordered Ag nanowires has slightly increases along the radius of the circle in the ring region, the degree of nanowire ordering has no obvious change in different position along the ring radius. This result indicates that Ag nanowires are aligned well along the circle radius in the large ring region. Indeed, alignment of Ag nanowires has been found to extend up to 4 cm² and seems to be limited by the volume of the droplet, on the basis of experiments carried out with volumes ranging from 1–10 μL.

In addition, no matter what volume of the droplet, the arrangement of Ag nanowires is random in the central region of the circle. The detail results of the arrangements of Ag nanowires in the central region are shown in Fig. S1.

Discussion

Based on the framework of shear flow, we theoretically analyze the factors controlling the alignment and the density changes of Ag nanowires in the ring region. Schematic diagrams are used to reveal the effect of the spreading on this special alignment as shown in Fig. 3(a). Different from the evaporation method⁸, the orientation of Ag nanowires is mainly occurs in the spreading process by a CCD device equipped on microscopy (see the Supporting Information). Specifically, the spreading microfluid near the substrate surface resembles a shear force and aligns the Ag nanowires in the spreading direction before they are immobilized on the substrate as shown in Fig. 3(a). Subsequently, some of the ordered Ag nanowires in the suspension are gradually sink onto solid substrate due to the gravity

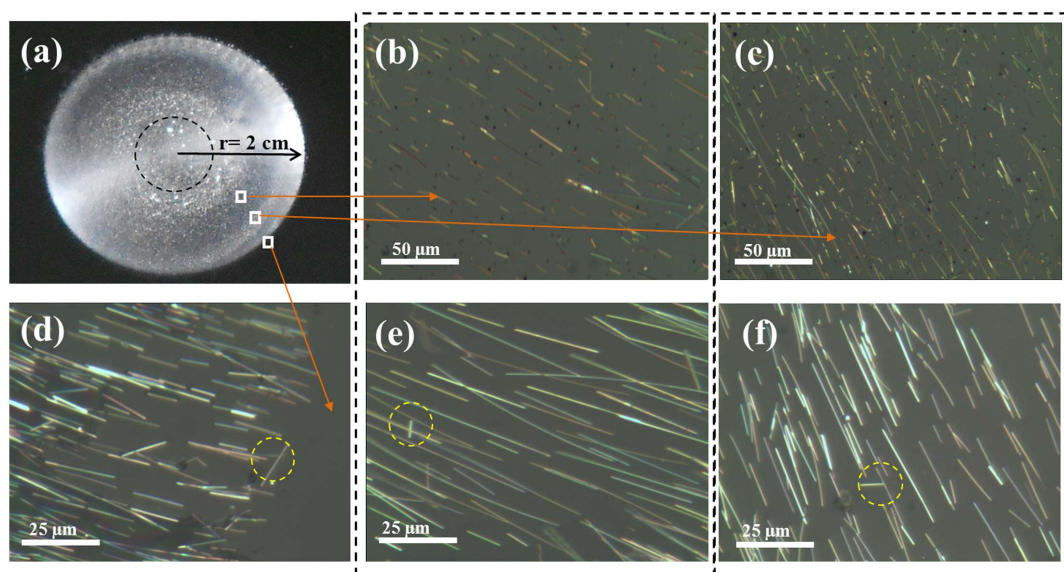


Figure 2 | Parallel assembly of Ag nanowires array. (a) Top view optical image of a circle shaped thin layer of Ag nanowires; (b) Optical microscopy image of Ag nanowires in the ring region; (c) Optical microscopy image little further away from (b); (d) Optical microscopy image of Ag nanowires in the edge region; (e), (f) Higher resolution of optical microscopy image of (b) and (c). Ag nanowires which are not well aligned are pointed out by yellow dashed circle. All optical microscopy images are obtained under bright field mode of microscope.

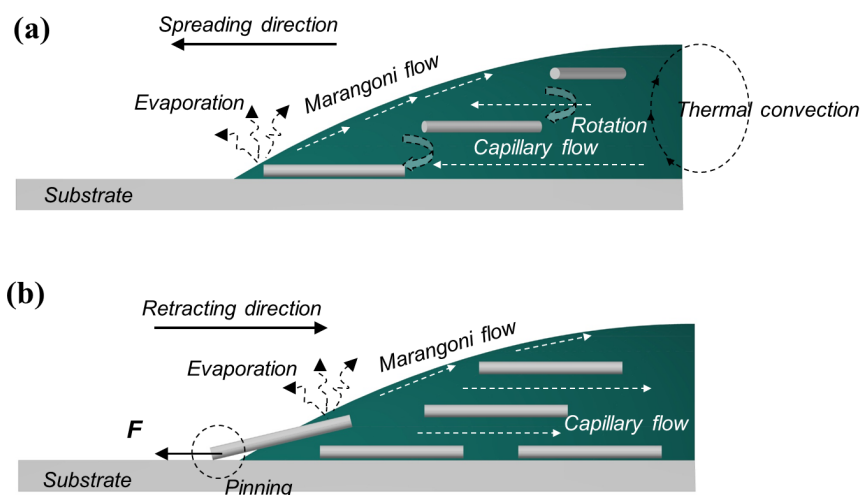


Figure 3 | Schematic of orientation of Ag nanowires during spreading and evaporation process. (a) Spreading directions of microfluid and the movements of Ag nanowires near the substrate during spreading process; (b) Retracting directions of microfluid and the movements of Ag nanowires at the initial of shrinkage of the suspension.

effect. And others are carried out by the spreading flow and sink on the substrate along the circle radius. Obviously, the spreading flow rate and the adhesion forces of the substrate which can be attributed to the van der Waals force between Ag nanowires and substrate surface are the most important factors that lead to the final alignment of Ag nanowires on solid substrate surface. On the equilibrium of the two factors, ordered Ag nanowires can be adhered and aligned on solid substrate. Although the adhesion forces of the substrate mainly depended on the contact area between Ag nanowires with substrate can be approximate as a constant, the spreading flow rate of the microfluid is decreased with the spreading radius and the duration of the spreading flow²². Based on the changes of the flow rate of the spreading microfluid, we could clearly understand the adhesion and alignment of Ag nanowires on solid substrate surface during the spreading process. At the initial stage of the spreading process, Ag nanowires are already well ordered in the suspension due to the high shear forces of the high rate of the spreading flow. However, under such high shear forces, the substrate cannot catch the ordered Ag nanowires out of the suspension and align onto its surface. Most Ag nanowires near the substrate are washed away by the fast spreading flow, which is proved by our CCD observation. As the spreading process proceeds, the spreading rate is greatly decreased with the spreading radius and flow duration. At this stage, Ag nanowires near the substrate are easily adhered and aligned on the substrate surface far away the central due to the decrease of the shear forces in the suspension. Thus, there is a small density change of ordered Ag nanowires along the spreading direction on the solid substrate surface (Fig. 2(b) and 2(c)). Because the Ag nanowires are already oriented in the suspension, the flow rate change seems have little influence on the alignment of Ag nanowires on solid surface during the spreading process.

In addition, large deviations of few Ag nanowires with respect to the flow direction (Fig. 2(d), 2(e) and 2(f)) can be attributed to the insufficient rotation of Ag nanowires near the substrate. In detail, some of Ag nanowires initially very close to the solid surface and then firmly adhere on the substrate that shear forces cannot rotate them during the spreading process. This irregular adhesion of Ag nanowires on silicon (glass) surfaces could be affected by the aspect ratio of Ag nanowires and the concentration of the suspension (discussed in the Supporting Information). Finally large deviations of few Ag nanowires with respect to the flow direction are left on the solid substrate surface.

Accompanied by the spreading process, there is always exists the high rate of evaporation on the suspension surface as shown in Fig. 3(a). Due to the evaporation of the suspension, the spreading process is quickly finished, which only takes 20–30 s. As the spreading process finished, the shrinkage process of the suspension thin film begins subsequently. The thin circle suspension film shrinks and vanishes rapidly from the edge to the center in only 10–15 s. During this process, standard Newton's rings can be clearly observed on the film as shown in Fig. 4. Obviously, as the film shrinks and vanishes rapidly from the edge to the center, the angle changes of the flow direction are 180 degrees (Fig. 3(b)). Ordered Ag nanowires in the edge of the suspension film are pulled out of the suspension by the pinning force F between the nanowires and the substrate. During this stage, for anti-Brown movement abilities of Ag nanowires in low shear force suspensions⁵ and the 180 degrees changes of flow direction in the suspension, the shrinkage of the thin film has little effect on the oriented arrangement of Ag nanowires. During this process, obvious Newton's rings emerge on the thin suspension film due to the rapid and uniform thinning of the suspension film (from several microns into near one hundred nanometers in only 3–5 s). As the thinning of the suspension film, Ag nanowires in the suspension are directly adhered on the substrate and cannot move by the thin film. Finally, as the Newton's rings disappear, a radial shaped alignment of Ag nanowires array is left on the substrate.

Through above analysis, the large area of Ag nanowires array formed on solid surface can mainly attributed to spreading shear flow and adhesion of the substrate during the spreading process. Compared with the evaporation method^{18,13,14}, in our case, the evaporation induced retracting of the suspension film has little effect on the alignment of Ag nanowires on solid substrate which shows significant differences.

By above spreading method, the obtained Ag nanowire arrays could meet small scope application in devices by direct transfer technology²³. For the needs of large scope of Ag nanowire arrays (about order of square centimeters) in one direction, we provide a simple device to transfer Ag nanowires on to a target substrate. A schematic diagram of the Ag nanowires transfer device is shown in Fig. 5. This device contains a connecting rod and rubber roller. A thermal release tape is adhered onto the surface of the rubber roller. When the connecting rod rotates, the rubber roller rotates due to rolling friction induced by the rotation of the connecting rod. The radial aligned Ag nanowires can be uniformly adhered and oriented in the same dir-

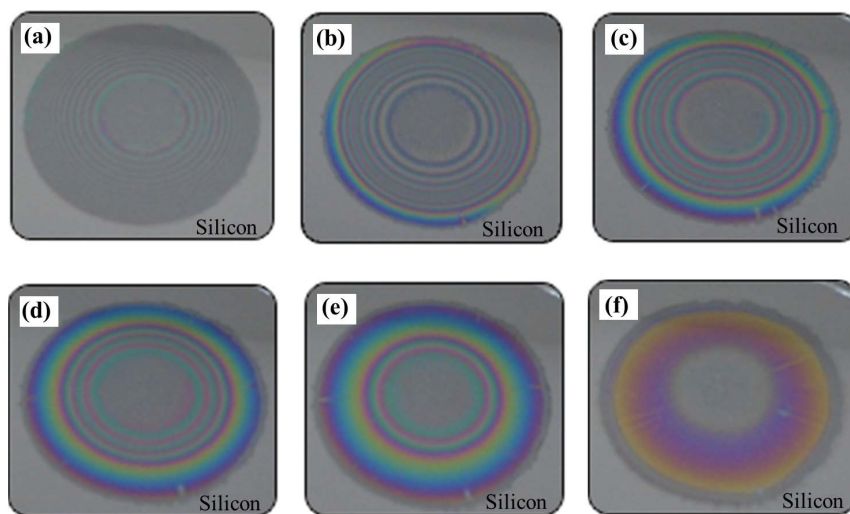


Figure 4 | Optical images of Newton's rings on silicon surface. (a) Newton's rings at the initial of the shrinkage process of the suspension thin film; (b) to (f) Newton's rings on silicon surface after 10 s, 20 s, 30 s, 40 s and 50 s.

action on the tape as shown in Fig. 5(b) and 5(c). The density of Ag nanowires can be controlled by the number of turns of the cylinder. Then, the large scope Ag nanowire array on the thermal release tape (shown in Fig. S2) can be further transferred onto a target substrate.

In summary, the spontaneous spreading of volatile droplet on solid surface are proved as an extremely easy, fast and economic way for Ag nanowires alignment on a solid surface. In the orientation process, we discovered that Ag nanowires are ordered by the spreading microfluid in the suspension and then adhered on the solid surface. Furthermore, the shrinkage of the suspension film induced by the evaporation has no obvious influence on the orientation of Ag nanowires, which shows great differences with that by the similar evaporation orientation methods. A simple device is designed to transfer and align the radial shaped oriented Ag nanowires into a target substrate into one direction. This work has provided a very efficient way for commercial production of nanowires arrays in a wide range of fields.

Methods

Preparation of Ag nanowires. Ag nanowires with average diameter of 200 nm and length of 30 μm were synthesized by the hydrothermal method. In detail, a specified

amount of silver nitrate (0.17 g), PVP (average molecular mass 360 k in terms of monomeric units) (0.2 g), sodium sulfide (7.2 mg) were dissolved in 20 ml ethylene glycol and stirred vigorously until to clear. The clearly solution was placed in a 50 ml teflon-lined stainless autoclave, and then heated to 160°C and remained for 5 h under autogenous pressure. After that, hoary turbid liquid were obtained when the autoclave was cooled to room temperature. Ag nanowires were centrifuged and washed twice with anhydrous ethanol.

Orientation of Ag nanowires on silicon (glass) surface. All the experiments were done in a normal atmospheric environment with natural air flow. The experiments were carried out at room temperature and there were no additional special conditions. The standard cleaning procedure of silicon and glass is adopted. The silicon and glass are first cleaned ultrasonically in baths of acetone for 10 min and then rinsed several times with deionized water. Thereafter, silicon and glass are dried by nitrogen. Pipettes are used to drop the droplets on solid substrate. In order to reduce the effect of impact flow and gravity flow on the alignment of Ag nanowires, the distance between the pipettes orifice and the silicon (glass) surface is controlled and fixed to be very small (3–5 mm). The diameter and volume of the droplets are simply controlled by the size of the pipette orifice. Generally, the diameter of the droplet can be controlled in the range of 1–4 mm and the volume in the range of 1–10 μL . Then the droplet spreads on the silicon (glass) surface and evaporates naturally on the substrate in the normal atmospheric environment.

Characterization. The morphology of the Ag nanowires was determined by field emission scanning electron microscopy (FESEM, JEOL Corp., Model JSM-6700F). The arrays of Ag nanowires and the alignment movie of Ag nanowires were observed using optical microscopy (Yongxiang corp., Model 10XB-PC).

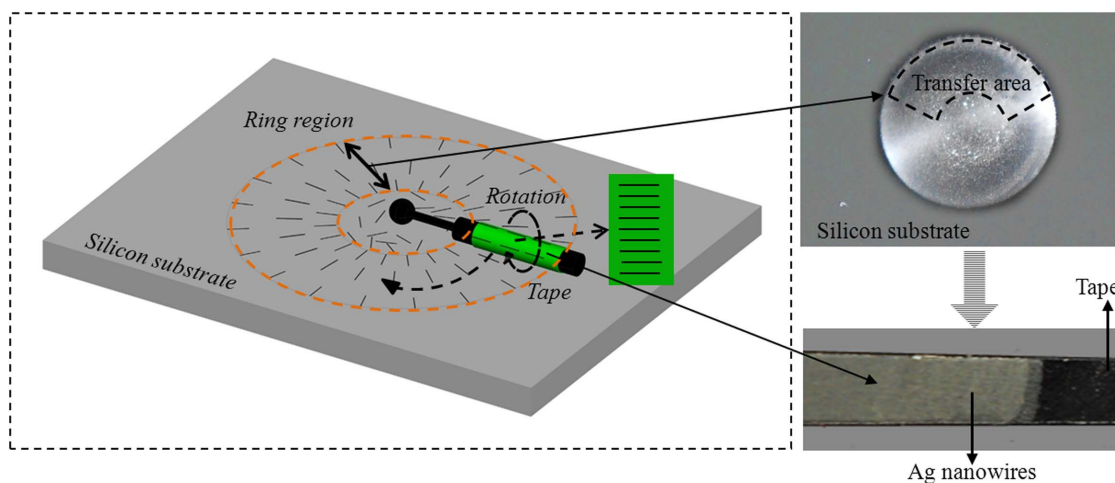


Figure 5 | Schematics of a simple device for the transfer of large scope of Ag nanowire array. Right: Optical image of the transfer area in the ring region and the transferred Ag nanowires on the tape.



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Author contributions

H.D., R.Q.D. and M.C.L. planned and experiment designed; H.D. wrote the manuscript draft; R.Q.D. did the experiments; H.D., R.Q.D., M.C.L., J.J.H., Y.F.L. and M.Y.T. co-revise the manuscript; H.D. and R.Q.D. processed data and prepared the figures; All authors reviewed the manuscript.

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