VIP Nanowire Devices Very Important Paper

DOI: 10.1002/anie.201408298

Manipulating Nanowire Assembly for Flexible Transparent Electrodes**

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Abstract: *Manipulating nanowire assembly could help the design of hierarchical structures with unique functionalities. Herein, we first report a facile solution-based process under ambient conditions for co-assembling two kinds of nanowires which have suitable composition and functionalities, such as Ag and Te nanowires, for the fabrication of flexible transparent electrodes. Then Te nanowires can be etched away easily, leaving Ag nanowire networks with controllable pitch. By manipulating the assembly of Ag and Te nanowires, we can precisely tailor and balance the optical transmittance and the conductivity of the resulting flexible transparent electrodes. The network of Ag nanowires which have tunable pitch forms a flexible transparent conducting electrode with an averaged transmission of up to 97.3% and sheet resistances as low as 2.7 Ω/sq under optimized conditions. The work provides a new way for tailoring the properties of nanowire-based devices.*

In contrast to rigid and opaque electrical devices, the successful fabrication of many modern optoelectronic devices including touch screens, organic light-emitting diodes (OLEDs), electronic displays, and solar cells, requires electrodes that are flexible, transparent, and with high conductivity, they should be designed to withstand high levels of bending without degradation of the electrical properties.[1] Flexible transparent electrodes combine and balance optical transparency and electrical conductivity providing the possibility to extract electrical carriers while transmitting light through the layer. To accelerate the application of flexible transparent electrodes, the pursuit of improving transmittance and simultaneously lowering sheet resistivity is necessary because these two critical parameters typically follow opposite trends. Although indium tin oxide (ITO) has been most widely used in optoelectronic devices traditionally, many reports have been published on how to overcome electrode brittleness, low infrared transmittance, and low abundance limit suitability, by using materials such as metal nanowires, graphene, and carbon nanotubes (CNTs) networks.[1a,2] However, thin films of CNTs and graphene exhibit sheet resistances and optical properties of 100–1000 Ω/sq at 80–90% optical transmittance which are still not good enough for most applications.[3] Thin films of metal nanowires, in comparison, hold great promise because of their high conductivity and optical transmittance. The transparent conductive electrodes based on random metal nanowires, however, still have many problems, such as the balance between optical and electrical conductivity, uniformity of the nanowire films, and their durability at different working conditions, as well as the electrical contact between the nanowires themselves. These limits call for tunable, novel, and scalable approaches to fabricate metallic network films.

Macroscopic-scale nanowire assemblies offer a wide variety of potential applications with improved performance and lower costs. Rational assembly strategies have been employed to prepare nanowire thin films in wafer scale for novel collective properties and device fabrication at a practical scale.[4] Manipulating nanowire assembly could allow the preparation of transparent conductive electrodes with well-defined nanowire structures which enable the tuning and tailoring the properties. Nanomaterials with surfactants surrounding tend to aggregate and search for their densest packings which is disadvantageous for their transparence.[5] So, the establishment of large-area nanowire networks with controllable pitch of the nanowire (the distance between two adjacent nanowires) at low costs remains a challenging task.

Herein, we report a new solution-based approach for manipulating nanowire assembly and fabricating large-area nanowire networks with tunable pitch (distance between two adjacent nanowires), which can be used to produce large-area flexible transparent conducting electrodes. Briefly, Ag nanowires and Te nanowires are co-assembled using the Langmuir–Blodgett (LB) technique, the Te nanowires are then selectively etched away leaving an Ag nanowire network with pitch tuned by the Te nanowires. Moreover, the Te nanowires used here as templates can be recycled. The resulting flexible transparent conducting electrode shows an averaged transmission up to 97.3% for the best transmitting network and sheet resistances as low as 2.7 Ω/sq, which is a better performance than an 80 nm thick layer of ITO sputtered on glass. The present work provides a new avenue for designing flexible nanowire electrodes for nano-devices with high-transmittance and low-resistance.

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[**] S.H.Y. acknowledges the funding support from the National Basic Research Program of China (Grants 2010CB934700, 2013CB933900, 2014CB931800), the National Natural Science Foundation of China (Grants 21401183, 21431006, 91022032, 912271032), and the Chinese Academy of Sciences (Grant KJZD-EW-M01-1). J.-W.L. is grateful for the Fundamental Research Funds for the Central Universities (WK2060190026).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408298.

Transmittance of the Ag nanowire monolayer is commonly studied but it lacks precise control. Herein, we combine structure design and chemical activity of the co-assembled nanowire films by manipulating the nanowire assembly to tailor the optical transmittance. Figure 1 a shows

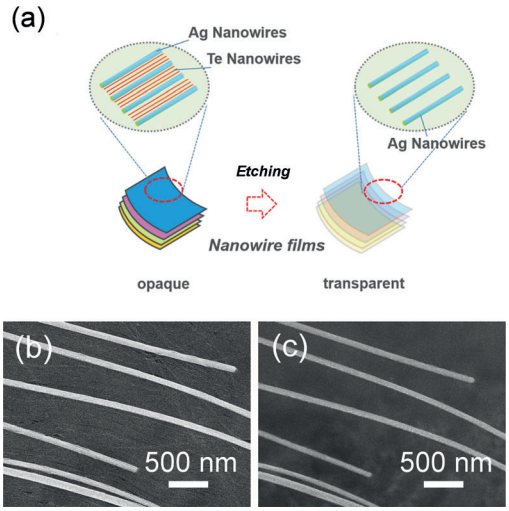

Figure 1. a) Schematic representation of a typical nanowire co-assembly process. b,c) SEM images of the before and after etching away the Te nanowires.

the proposed strategy for the fabrication of flexible transparent electrodes. In the first step, Te nanowires with a diameter of 7 nm and lengths of hundreds of micrometers and Ag nanowires with diameters of 50 nm lengths of 5 μm were synthesized as described previously (Supporting Information, Figure S1–S4).[6] Then, the two kinds of nanowires which have different reaction activities are co-assembled by Langmuir–Blodgett (LB) technique,[4d,7] which is a low-cost and scalable approach for forming ordered nanowire monolayer or multilayer nanowire networks, on polyethylene terephthalate (PET) substrate. In the third step, Ag nanowire monolayer can be prepared by removal of the reactive ultrathin Te nanowires, the pitch of the nanowire network is determined by the Te nanowires allowing a dramatic but flexible tuning of the transmittance of nanowire films. Ultrathin Te nanowires with a diameter of 7 nm are rather reactive and can be used as excellent templates to synthesize other one-dimensional materials, such as telluride and even noble-metal nanowires.[8] The stability of the Te nanowires in water in the presence of oxygen has been systematically investigated.[9] So, the Te nanowires located in the nanowire assemblies can be easily oxidized into soluble TeO_3^{2-} in the presence of oxygen in an alkaline environment. After removal of the Te nanowires, the pristine Ag nanowire assemblies can be perfectly maintained and this process is very reproducible. Figure 1 b and Figure 1 c show that the alignment of the Ag nanowires was unchanged after etching away of the Te nanowires. Moreover, ultrathin Te used for separating Ag nanowires could be recycled by a simple reducing reaction with good reproducibility and conversion yield about 80 % (Supporting Information, Figure S5). These reactions involving Te can be formulated as in Equation (1).

$$O_2 + Te + 2\,OH^- \rightarrow TeO_3^{2-} + H_2O$$
$$TeO_3^{2-} + N_2H_4 \cdot H_2O \rightarrow Te + N_2 + 2\,H_2O + 2\,OH^- \quad (1)$$

The successful design of high-quality flexible transparent electrodes is strongly dependent on their transmittance, electrical conductivity, and the balance between their transmittance and conductivity. After tailoring the transmittance of the nanowire monolayer, more complex structures could be designed to explore their electrical conductivity. The process for fabricating the flexible transparent electrodes is illustrated in Figure 2 a. Two-layer nanowire networks with mesh-like structures formed by depositing with expected crossing angles by the LB technique, allowing a flexible adduction of their transmittance while retaining a high-performance electrical conductivity.[10] As shown in Figure 2 b, highly flexible and transparent Ag nanowire films on PET substrate can be fabricated on a large scale. Figure 2 c,d show the SEM images of the Ag and Te nanowire co-assemblies. Then, by loading the other nanowire monolayer on the first one (Figure 2 e), the transmittance of the nanowire films becomes much better when the Te nanowires are removed (Figure 2 f). It was found that the well-defined Ag nanowire films with controlled nanowire pitch are optically transparent and mechanically flexible and robust. Compared the optical transmission spectra of the randomly and ordered arranged nanowires with the same nanowire density, and the performance of the disordered nanowire films are unstable, and the reproducibility is poorer (Supporting Information, Figure S6a and S6b).

Owing to the different components of two kinds of nanowires in the present co-assembly systems, the pitch of the Ag nanowires is controlled by the more reactive Te nanowires, thus forming Ag nanowire networks with controllable transmittance. However increasing the number of metal nanowires will decrease the resistance, however this also results in a decrease in the optical transmission of the nanowire network (Figure 3 a). To evaluate the flexibility of the nanowire assembly flexible transparent electrodes, we tailored the pore area of the Ag nanowire assemblies to balance the transmittance and conductivity. As described previously, nanowire networks can be fabricated by LB technique.[10a] The pitch of the well-aligned Ag nanowires can be tuned by the reactive Te nanowires. From Figure 3 b to Figure 3 g, the molar ratios of the Ag nanowire and Te nanowire assemblies can be controlled from 1:400, 1:350, 1:300, 1:250, 1:200, and 1:100. It was found that the pore area of the Ag nanowire assemblies decreases when the amount of Te nanowires is decreased in the co-assembly process. So, the pore area of the Ag nanowire films ranges from hundreds of square micron (Figure 3 b) to hundreds of square nanometers (Figure 3 g). Correspondingly, the transmittance of nanowire networks can be tuned from 97.3 % to 92 %, 90 %, 85 %, 80 %, and 73.8 % (Figure 3 h).

Simultaneously, the conductivity of the nanowire films changed from 40 Ω/sq to 20 Ω/sq, 13 Ω/sq, 7 Ω/sq, 5 Ω/sq and 2.7 Ω/sq (Inset in Figure 3 h). Silver is widely used for flexible transparent electrodes because of its excellent conductivity

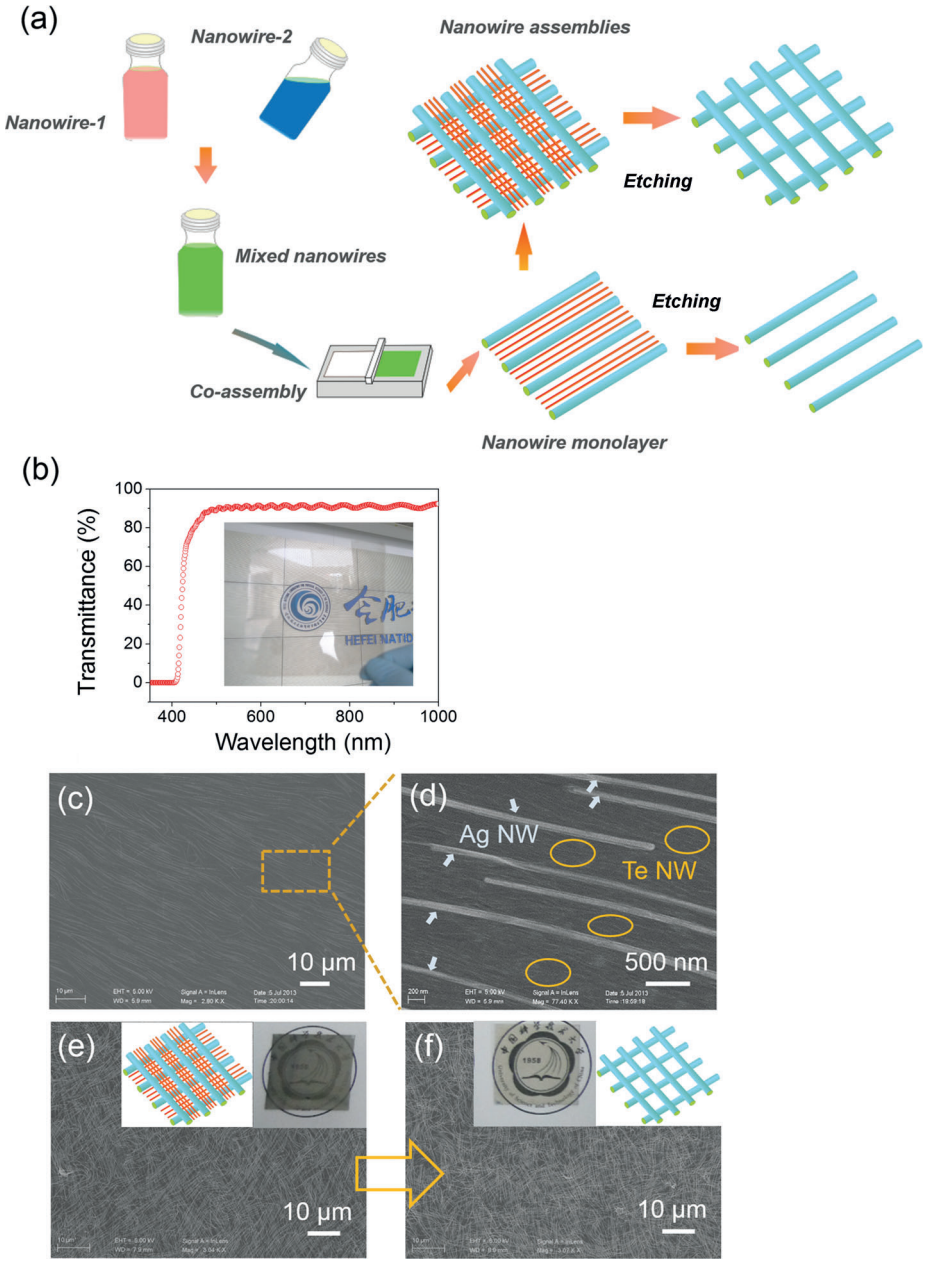

Figure 2. a) Schematic illustration of nanowire assembly to make flexible transparent electrodes. b) The optical transmittance spectra of the nanowire-based transparent electrodes (Inset: photograph of a flexible transparent electrode). c,d) SEM images of nanowire co-assemblies, monolayers of Ag and Te nanowires at different magnifications. e,f) SEM images of the nanowire assembled networks before and after etching away of the Te nanowires Insets: schematic illustration of the nanowire assemblies and photographs of the corresponding films.

and low optical loss in the visible range.[11] Traditionally, Ag nanowire films and networks are usually used as flexible, transparent electrodes. However, the methods usually lack tailoring between the optical transparency and electrical conductivity.[12] Figure 3i shows the transmittance of the Ag nanowire electrodes with various sheet resistances Rs (at 550 nm).[12b,c,e,f,13] As we know, the electrodes based on the thicker and longer Ag nanowires result in better performance in transmittance and conductivity. Because of the nanowire assembly strategy employed the electrodes in the current work exhibited one of the best performances.

The flexibility and stability are two important properties for long-life flexible transparent electronics. Figure 4a,b illustrate the electrical performance of the electrodes under the cyclic mechanical deformations. We evaluated the folding capability of the Ag nanowire flexible electrodes by measuring resistance with respect to bending radius which was carried out with a high-precision mechanical system (Instron 5565A) and a Keithley 4200 SCS in a clean, metal-shielded box. Figure 4a shows that the resistance value was maintained at a constant value after the initial decrease during the cyclic bending test, even at a bending radius of 2.0 mm. To test the stability, the flexible electrodes still show a good conductivity with an electrical resistance only changing from 18 Ω to 21 Ω after more than 3000 bending cycles revealing that the conductance of the Ag nanowire electrode was hardly affected by bending stress indicating its excellent reversibility (Figure 4b). This initial resistance change may have been caused by electrical joule heating and annealing during the long time test. Unlike the fragile ITO electrode, the flexible transparent electrode increases a device's lifetime and broadens their applications.

Furthermore, we also test their mechanical properties and electrical properties immersion in liquid. After the nanowire assembly, the nanowire electrodes kept their conductivity even when the device was twisted in water or ethanol (Figure 4c, see also the Video S1 in Supporting Information). To validate the practical application of current technology, fabricated Ag nanowire transparent electrodes were applied to a touch panel screen demonstration as shown in Figure 4d (see also the Video 2 in Supporting Information), writing the characters "USTC" and "Yu lab". Compared with the commercial ITO-coated touch screen which requires an expensive vacuum process, in the present case, all the flexible electrodes were fabricated by solution processes and show tunable performance.

In summary, we have successfully taken advantage of manipulating nanowire assembly to precisely tailor the optical transparency and electrical conductivity of the flexible

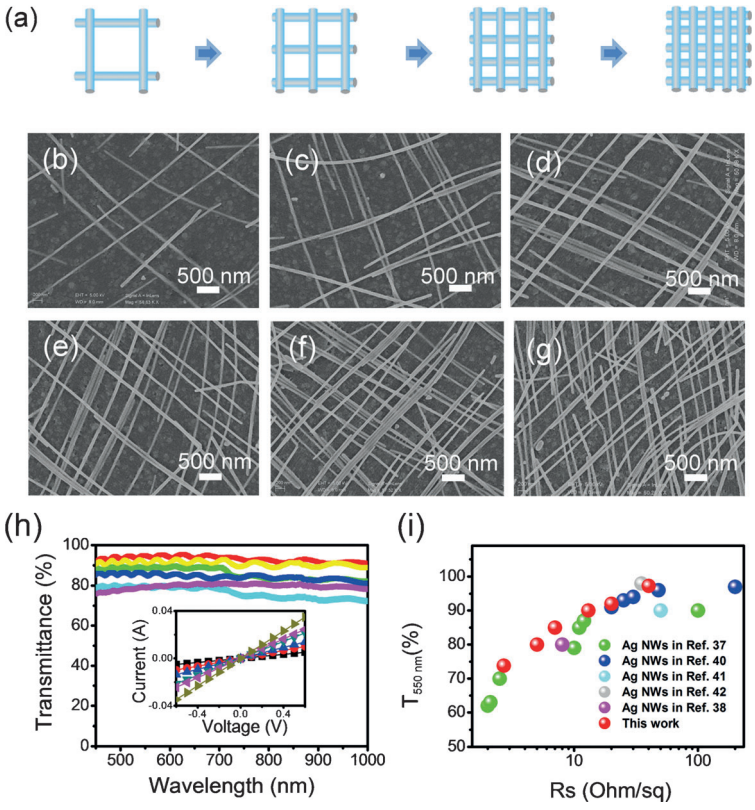

Figure 3. Flexible transparent electrodes based on the well-aligned Ag nanowire films. a) Illustration of the pore area of the nanowire networks. b–g) SEM images of well-defined Ag nanowire networks with different pore areas of the nanowire assemblies; see text for details. h) The optical transmittance spectra corresponding to the samples from b to g (the transmittance gradually changed from high to low). Inset: the current–voltage characteristics (the conductivity changing from low to high) corresponding to the samples from b to g, respectively. i) Sheet resistance versus optical transmission (at 550 nm) for Ag nanowire networks prepared by different methods.[12b–f,13] Note that the transmittance does not include the transmittance of the PET substrate.

nanowire electrode by co-assembling Ag nanowires with Te nanowires by Langmuir–Blodgett technique, then Te nanowires can be etched away easily, leaving Ag nanowires with controllable pitch. The Te nanowire used as templates can be recycled by a simple reaction. The flexible transparent conducting electrode fabricated by the nanowire co-assembly approach shows an averaged transmission up to 97.3% for the best transmitting network and sheet resistances as low as 2.7 Ω/sq which have better performance than an 80 nm thick layer of ITO sputtered on glass. This versatile strategy will provide possibilities for the large-scale fabrication of flexible and transparent electrodes exhibiting a good compromise between optical transparency and electrical conductivity.

Experimental Section

All chemicals are of analytical grade and were used as received without further purification.

Synthesis of Ag nanowires: All chemicals and solvents were purchased from Shanghai Chemical Reagent Co. Ltd. and used without further purification. Uniform Ag nanowires with an average diameter of 60 nm were prepared by the polyol process method reported previously.[6a] In the typical synthesis, polyvinylpyrrolidone (PVP, $M_W \approx 40000$; 1.76 g) was added into glycerol (57 mL) in a round-bottomed flask under gentle stirring and the solution kept at 85 °C for 1 h to form a homogeneous solution. After cooling to the room temperature naturally, $AgNO_3$ powder (0.474 g) was added into the solution. After that, a NaCl solution (17.7 mg of NaCl dissolving in 0.15 mL of deionized water and 3 mL of glycerol) was added into the flask. The temperature increased from room temperature to 210 °C in 20 min under continuous stirring, the heating was stopped immediately. Then deionized water (60 mL) was added into the flask and the temperature allowed to drop to room temperature. The solution turned from pale white into light brown, red, dark gray, and eventually gray-green. The solution was centrifuged to remove the excess PVP, and then the Ag nanowires were collected and dispersed into an aqueous solution.

Synthesis of Te nanowires: The synthesis of uniform Te nanowires was described previously.[6b,9b] Briefly, Poly(-vinyl pyrrolidone) (PVP, Shanghai Reagent Company, $M_W \approx 40000$; 1.0000 g) and Na_2TeO_3 (0.0922 g) were added into double distilled water (33 mL) under vigorously magnetic stirring to form a homogeneous solution. After that, hydrazine hydrate (85%, wt%; 1.67 mL) and aqueous ammonia solution (25–28%, wt%; 3.33 mL) were added into the stirred solution. Then, the container was closed, stirring and maintained at 180 °C for 3 h. The autoclave was cooled to room temperature naturally.

Co-assembly of Ag and Te nanowires by the Langmuir Blodgett (LB) techniques: The assembly of well-defined nanowire networks was by using a modified Langmuir–Blodgett technique described previously.[10] The nanowire assemblies were prepared at room temperature in a Langmuir–Blodgett trough (Nima Technology, 312D) using Millipore Milli-Q water (resistivity 18.2 MΩ cm) as subphase. The freshly prepared Te nanowire solution (1 mL; 0.47 mM) was centrifuged after adding acetone (2 mL) and washed with absolute alcohol and double distilled water several times. Then, the Te nanowires were dispersed into a stirred solution of *N*,*N*-dimethylformamide (DMF; 0.5 mL) and $CHCl_3$ (0.5 mL). Ag nanowire suspension (0.046 mM; 0.1 mL or 0.2 mL, 0.25 mL, 0.3 mL, 0.35 mL, 0.4 mL) was added into the Te nanowire solution to form a homogeneous solution at room temperature. A 50 μL syringe was used to dispense mixed nanowire suspension onto the water subphase drop by drop. 30 min later, the nanowires surface layer was compressed with a compression rate of 20 $cm^2 min^{-1}$. The surface pressure was kept constant as soon as the fold formation that paralleled to the barrier direction occurred, while the surface pressure was monitored with a Wilhelmy plate. The nanowire networks were obtained by depositing two layers of aligned nanowires into mesh-like structures with crossing angles. The Te nanowires of the co-assemblies can be removed by treatment with electrodes in 1M of NaOH solution at room temperature for 2 h. The color of the electrodes turned from dark blue into light yellow and eventually transparent. After washed with ethanol and water, the electrode was dried by blowing N_2.

Touch-screen device fabrication: The touch-screen device was rebuilt from a commercial product from Hanvon Electronics which was described previously.[1e] The 2.8-inch device consisted of an ITO electrode on a PET film and a piece of ITO glass, which were separated by square arrays of polymer spacer dots. In the rebuilt device, the ITO/PET film was replaced with well-defined Ag nanowire network on PET substrate. The connection between the Ag nanowire networks with the commercial controller which interfaced with the computer is carried out by patterning a copper circuit with the aid of a plastic hard mask.

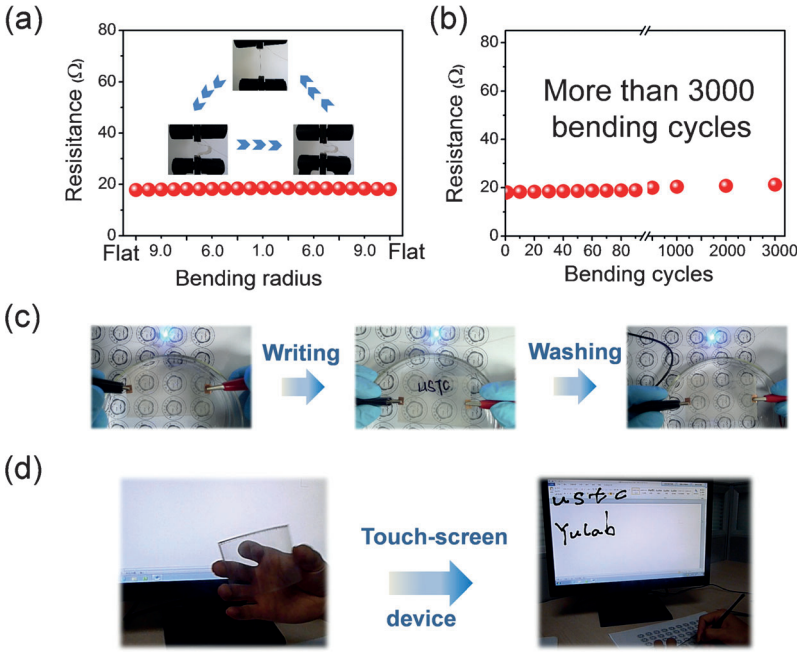

Figure 4. Mechanical flexibility and stability of the transparent electrodes. a,b) Electrical resistance as a function of the bending cycles at a maximum bending radius of 2.0 mm. Inset: photograph of the bending process of Ag nanowire electrodes. c) Stills from video clips (see Supporting Information) of the Ag nanowire film electrodes, immersion in liquid to show their mechanical properties and electrical properties. A blue LED light with a battery pack was connected by the flexible transparent electrodes, the LED remains lit throughout the immersion/bending process. d) Video clips of high performance of the touch panel based on an Ag nanowire assembled electrode. Text hand written on the touch panel is transferred to the computer screen.

Instruments: The conductivity (sheet resistances) of the nanowire films were investigated with a PM5 Analytical Probe System (Cascade Microtech, Inc.) and a Keithley 4200 SCS in a clean, metal-shielded box at room temperature in air with a four-point probe configuration to eliminate contact resistance. The transmittance measurement and UV/Vis spectra were recorded on UV-2501PC/2550 at room temperature (Shimadzu Corporation, Japan). Field-emission scanning electron microscopy (FESEM) was carried out with a field emission scanning electron micro-analyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV).

Received: August 16, 2014
Published online: October 3, 2014

Keywords: assembly · flexible electrodes · nanowires · silver · transparent electrodes

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