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2016

Kang, W., Lin, M.-F., Chen, J., & Lee, P. S. (2016). Highly transparent conducting nanopaper for solid state foldable electrochromic devices. *Small*, 12(46), 6370-6377.
doi:10.1002/smll.201600979

<https://hdl.handle.net/10356/140424>

<https://doi.org/10.1002/smll.201600979>

This is the accepted version of the following article: Kang, W., Lin, M.-F., Chen, J., & Lee, P. S. (2016). Highly transparent conducting nanopaper for solid state foldable electrochromic devices. *Small*, 12(46), 6370-6377, which has been published in final form at <https://doi.org/10.1002/smll.201600979>. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

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DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Highly Transparent Conducting Nanopaper for Solid State Foldable Electrochromic Devices

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Keywords: nanopaper, transparent conductive electrodes, foldable electronic devices, electrochromics

It is of great challenge to develop a transparent solid state electrochromic device which is foldable at the device level. Such devices require delicate designs of every component to meet the stringent requirements for transparency, foldability and deformation stability. Meanwhile, nanocellulose, a ubiquitous natural resource, is attracting escalating attention recently for foldable electronics due to its extreme flexibility, excellent mechanical strength and outstanding transparency. In this article, transparent conductive nanopaper delivering the state of art electro-optical performance is achieved with a versatile nanopaper transfer method that facilitates junction fusing for high quality electrodes. The highly compliant nanopaper electrode with excellent electrode quality, foldability and mechanical robustness suits well for the solid state electrochromic device that maintains good performance through repeated folding, which is impossible for conventional flexible electrodes. A concept of camouflage wearables is demonstrated using gloves with embedded electrochromics. The discussed strategies here for foldable electrochromics serve as a platform technology for futuristic deformable electronics.

1. Introduction

Electrochromism is defined as the reversible change of optical modulation under supplied voltage.^[1] Reversible electrochemical redox reactions are required for electrochromism during which the inter-valence charge transfer is reflected as the change of color. Electrochromism has been frequently utilized for applications such as smart windows, anti-glare mirrors, paper-like display etc. Typically, conventional electrochromism is essentially based on rigid glass substrate, which has substantially limited its application range. On the other hand, deformable electronic devices with desired functionalities are attracting great attention and interest from researchers recently due to their ability to maintain the physical integrity under bending or even folding and stretching.^[2] Foldability, the extreme form of mechanical bending, as one important aspect of deformable electronics is now being keenly sought after for potential foldable smart phone displays^[3] with the possibility of endurance to fracture, adjustable conformation, good portability etc.^[4] However, freely foldable electrochromics have rarely been reported,^[5, 6] and none for a solid state transparent electrochromic device that folds on the whole device level, which requires a careful design of every component to be foldable and transparent. Here, fully foldable electrochromism has been realized, with promising potential applications for the next-generation smart displays such as foldable screen, color switchable textile and camouflage clothing etc.^[7] To realize a well-functioning foldable electrochromic device, two crucial components have to be carefully designed, the first of which is the transparent conducting electrodes (TCEs). TCE is one indispensable element for various optoelectronic applications such as solar cell,^[8] touch panel,^[9] light-emitting diodes,^[10, 11] electrochromics^[12] etc. The current TCE market is largely dominated by Indium Tin Oxide (ITO) due to its high conductivity and transparency and stability. However, the problems of scarcity of Indium, fluctuating cost, brittleness under deformation, have prompted an urgent need to find alternative materials for emerging and futuristic devices.

Besides, its brittle nature renders ITO totally not applicable for any extremely flexible applications.^[13] Existing TCE substitutes for ITO include carbon nanotube,^[11, 14] graphene,^[9, 15] metal grids,^[16] metallic wires network,^[13, 17, 18] , **conducting conjugated polymer**^[19-22] and hybrid electrodes.^[23, 24] Of all these, metallic wire based transparent conducting electrodes are showing great potential with high conductivity and strong endurance to deformations like stretching, bending and even folding due to its one dimensional morphology with high aspect ratio that guarantees constant interconnection without rupture under external forces.^[23, 25] **Although conducting conjugated polymers like PEDOT:PSS and PANI bear intrinsic flexibility which makes them appealing for deformable electronic applications, currently the conductivity of such electrodes remain to be improved in order to compete with metallic nanowire based electrodes.**

Ag nanowires percolating TCE representing this type is now being actively developed for deformable applications. Methods to improve the inter-wire junction condition are actively pursued so as to produce high quality Ag nanowire based TCEs^[26-28] to replace ITO and cater for the stringent requirement of next generation devices. Besides, techniques to protect the conducting elements from dislodgement during external deformations have to be urgently developed for a stable performance of deformable electronics.^[17]

Another major component for a foldable device is the delicate choice of foldable substrate that holds the conducting elements. The idea of adopting nanocellulose for paper electronics has lately stirred great excitement. Conventional flexible transparent conductive electrode substrates have been dominated by plastics such as polyethylene terephthalate (PET), polyimide (PI) or polycarbonate (PC). Nanocellulose gains an edge over these petroleum based polymers due to its strong mechanical strength, ubiquitous abundance, biocompatibility and tunable surface properties etc.^[29] The small size of the nanofibril leads to a large fiber to fiber interaction area

and correspondingly high overall mechanical strength.^[30] Besides, the small dimension of the fibers that is way much smaller than the visible light wavelength greatly reduces the forward and back light scattering.^[8, 31] This makes the nanopaper much more transparent than a conventional paper. Apart from these advantageous properties, nanocellulose possesses an excellent thermal stability ($>180\text{ }^{\circ}\text{C}$) and low coefficient of thermal expansion of $5\text{-}10\text{ ppm K}^{-1}$.^[32]

In this report, transparent nanopaper with outstanding mechanical deformation ability that folds to an extreme extent with radius below $10\text{ }\mu\text{m}$ is demonstrated. To pair with such extreme flexibility, Ag nanowires network is adopted as the conductive layer due to its outstanding mechanical compliance to accommodate deformation through the nanowire inter-slide mechanism. As such, the prepared conducting nanopaper is endowed with excellent foldability that is unreachable for conventional flexible electrodes. The high surface free energy of nanocellulose is leveraged in the nanopaper transfer method to obtain the conductive electrode. Not only is the transfer process easily facilitated but also a “kinked” structure can be obtained. Such structure is beneficial for improved junction that leads to a state of art electro-optical performance for nanowires based electrode with $10.5\text{ }\Omega/\text{sq}$, 94.6% . Besides this, the delamination issue of Ag nanowires is solved by transferring an additional SWCNT layer on top of the electrode to anchor the Ag nanowires. This improves the robustness of the electrode and makes the electrode feasible for the foldable electrochromic application.

2. Results and Discussion

Tempo assisted oxidized cellulose nanofibril (TCNF) as the nanocellulose source was adopted. The TCNF is very finely liberated with a fiber diameter of around 10 nm as shown in **Figure 1a**. The fine fibers form a much denser film compared to a Kimwipes paper of a few tens of micrometer in fiber diameter (Figure 1b). The dense film eliminates the pores and air cavity and

thus further reduces scattering.^[33] The TCNF nanopaper is highly transparent as shown in the photograph in Figure 1c. The transparency of the nanopaper (ca. 90.2% at 600 nm) is comparable to a glass slide (ca. 90.8% at 600 nm) in the visible range (Figure 1d) while showing a superior optical transmittance in the ultraviolet range with the absence of the low end absorption inherent in glass.^[10] Compared to the physically liberated cellulose nanofibril (PCNF),^[5] TCNF with the presence of surface carboxylic group is more well separated.^[34] This leads to a uniform composition of the fabricated nanopaper with low surface roughness (RMS=6.3 nm, Figure S1) and low scattering angle (1.06 °, Figure S2), rendering the TCNF nanopaper ultra clear under deep views (Figure S2). Notably, the measured haze value reduced dramatically from 83.7% for the PCNF nanopaper to 3.6% for the uniform TCNF nanopaper.

The TCNF nanopaper serves as a promising foldable substrate with its high transparency and low haze. To develop it into TCEs, the conducting function is imparted with the fabrication of kinked Ag TCE and SWCNT@Ag TCE using the nanopaper transfer method (experimental section and Figure 1e).

For the transferred Ag nanowire TCE, we observed strongly interacted junctions between adjacent nanowires that form a kinked nanowire structure as indicated in the circles of **Figure 2a**. For the SWCNT@Ag TCE, the kinked structure for the Ag nanowire is also observed (Figure 2b) and we found the SWCNTs mount over the Ag nanowires and anchor them tightly to the nanopaper substrate as shown in Figure 2c. Besides, the SWCNTs bridge the adjacent Ag nanowires and fuse them tightly as a bundle. For percolating type transparent conductive electrodes, the inter-wire junction resistance is the limiting factor that determines the conductivity.^[18, 28] Weak junction interaction severely impedes the conductive path and the overall conductivity of the percolating network. Some efforts have been channeled into reducing

the junction resistance to improve electrode conductivity such as Ag nanowire junction fusion by graphene oxide^[26], laser welding^[35], or monolayer graphene coverage for improved conduction^[36] etc. These methods are not effective enough to achieve high quality conductors^[13] ($T > 90\%$, $R_s < 10 \Omega/\text{sq}$) or the process is too cumbersome to operate. Our facile TCNF transfer method introduced here readily realized the inter-wire fusion for high quality TCE through a facile transfer technique without complex post treatment. Even for the kinked Ag nanowire TCE without SWCNT, the junctions are well fused together. This is attributed to the ultra-fine size of the TCNF gel which forms a conformal 3D coverage on the loosely packed Ag nanowires during filtration (Figure 2 d and e). When the water evaporates during the drying process, the strong cohesion induced by the hydrogen bonding interaction between nanofibrils and the large surface tension of the TCNF would enact the formation of a flat surface. This in-plane motion stretches the loosely packed out-of-plane Ag nanowires (Figure 2e) to the same nanopaper surface after drying and resulted in the kinked structure (Figure 2f).

The well fused junction in the kinked Ag TCE tremendously improved its conductivity by about 14 times (Figure 2I) in the low percolating end ($44.1 \Omega/\text{sq}$, 96.6% transmittance), as compared to the PCNF Ag TCE ($630 \Omega/\text{sq}$, 96.4% transmittance)^[5] because of the stronger interaction between Ag nanowires at the fused junction. This leads to a more efficient conduction path of the Ag network which greatly impacted this low percolating regime that is sensitive to junction resistance. When the SWCNT bridging with the Ag nanowires at the junction is introduced in the SWCNT@Ag TCE, the sheet resistance of the network is further reduced as shown in Table 1. To optimize the density of SWCNT for the best conductivity, diluted SWCNT suspension of different areal densities (D) is incorporated (experimental section). Ag nanowires with fixed areal density at M_1 (83 mg/m^2) and M_2 (111 mg/m^2) were selected separately to study the

influence of SWCNT on the sheet resistance as shown in Figure 2g. Both samples showed the same trend with the lowest sheet resistance obtained at 0.5D of SWCNT. This leads to the important finding that the bridging effect was levelled off after the critical point at 0.5D of SWCNT. Continued increasing of SWCNT amount would not further reduce junction resistance while instead, increases the roughness of the surface that is detrimental for a tight packing of the Ag nanowire network as evidenced in Figure S3. Thus, the sheet resistance of the samples beyond the optimal density would start to increase. Notably, for the sample with a lower areal density M₁, a higher amplitude of improvement in sheet resistance is clearly seen. This corroborates that for the less percolating network regime, the fewer number of junctions governs the overall conductivity and are more sensitive to the bridging by SWCNT.

When different amount of Ag nanowire is transferred, the sheet resistance and correspondingly the transparency would differ as reflected in Figure 2h and Figure S4. To determine the quality of the TCE fabricated from this nanopaper transfer technique, figure of merit ($F.O.M = \frac{\sigma_{dc}}{\sigma_{op}}$), derived from equation 1 is adopted.^[37-39]

$$T = (1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0}{\epsilon_0}} \frac{\sigma_{op}}{\sigma_{dc}})^{-2} = (1 + \frac{188.5}{Rs} \frac{\sigma_{op}}{\sigma_{dc}})^{-2} \quad (1)$$

σ_{dc} , σ_{op} , μ_0 , ϵ_0 refers to DC conductivity, optical conductivity, permeability of free space, permittivity of free space respectively. We observed an excellent F.O.M of 1055 for the Ag

TCNF transparent conductor (Table 1). The onset of full percolation starts around 5.09 Ω/sq when the conductivity of the percolating network reaches the bulk state that leads to the saturation of F.O.M.^[18, 28] To study the effect of SWCNT bridging on sheet resistance

improvement, we define the Improvement Factor (I.F) as $I.F = R_{s\_Ag} / R_{s\_SWCNT@Ag}$ as tabulated in Table 1. It is clearly shown that at the low percolation end, the I.F is larger because the junction

resistance as the determinant for overall conductivity changes sensitively with the addition of SWCNT. Then the I.F value falls close to 1 after the point of 5.09 Ω/sq , which corresponds well to the F.O.M trends after full percolation, that the overall conductivity becomes insensitive to the junction fusion since sufficient conduction pathways have been constructed. Overall, both electrodes deliver excellent qualities with kinked Ag TCE of 10.5 Ω/sq , 94.6% transmittance and SWCNT@Ag of 7.92 Ω/sq , 90.9% transmittance. Their performance is compared with some important work on high quality non-ITO TCEs in Figure 2I. The kinked Ag as well as SWCNT@Ag is positioned among TCEs of the best quality with especially kinked Ag showing the state of art electro-optical performance. Meanwhile, SWCNT@Ag gains an indispensable advantage over kinked Ag in that the protection from SWCNT anchoring prevents Ag from peeling in device applications which would be discussed later.

1D Ag nanowire and SWCNT with the inter-sliding mechanism promotes good interconnection upon strain, the soft and ductile nanowire allows it to conform to the deformed substrate without delamination.^[5] We define the folding angle as -180° when the electrode is folded face to face while the folding angle is defined as 180° when folded back to back (**Figure 3a**). The sample subjected to the folding test bears a thickness of around 8 μm and the bending radius is around 6 μm (Figure S5).

For both folding directions, the major sheet resistance changes occurred in the first 100 folding cycles and it is more or less stabilized in the following cycles for the SWCNT/Ag electrodes. The sheet resistance increased slightly by about 8.8% and 12.7% for -180° and 180° folding respectively after 500 extreme folding cycles with 6 μm bending radius (as shown in Figure 3b).

The asymmetrical change of the resistance is related to the different types of strain occurred on the nanopaper electrode. Convex folding (180°) leads to a tensile strain of the Ag nanowires

while concave folding (-180°) results in a compressive strain. Under the tensile strain, the Ag nanowires would be stretched and tend to align towards the tensile direction through inter-sliding^[25, 40] and this deteriorates the interconnection between nanowires and leads to the increase of the resistance.^[26, 41] For the concave folding, a compressive strain is applied to the conductive layer. Similarly, the conductive network would tend to align, but towards the direction perpendicular to the compressive direction. At the same time, the Ag nanowires network would be more compact under compression with the nanowires pushed tighter for a better contact.^[42, 43] The combined factors results in a smaller compromise of the resistance under concave folding and this leads to the anisotropic resistance change. In comparison, ITO/PET slightly bent to a radius of 10 mm was seen to suffer 500% increase in sheet resistance in 20 bending cycles.^[13] The strong preservation of the conductivity through these repeated folding is revealed from the FESEM images in Figure 3c and d. The Ag nanowires attach firmly to the TCNF substrate and the ductile metal wires deform in a conformal manner in response to folding without delamination. A circuit that connects LED lights with the SWCNT@Ag electrode is demonstrated in Figure 3e and f. The conductivity is maintained even after crumpling of the hybrid nanopaper TCE as reflected by the constant lighting of the LEDs.

A solid state foldable electrochromic device was fabricated on the SWCNT@Ag TCE. To achieve full foldability of the electrochromic device, every single component that comprises of the device has to be carefully designed to be foldable. For the active electrochrome, Ethyl Viologen Diperchlorate (EV^{2+}) which is an electrochromic water soluble small molecule was chosen for optical modulation. To pair with EV^{2+} to complete the reaction, Sodium Anthroquinone-2-sulfonate (AQS), an electrochemically active redox mediator was selected. The overall reaction can be simply described in equation 2.

To make a solid state device, a slime-making technique utilizing borax and PVA is adopted.^[44, 45] PVA and borax dissolved in water would interact strongly through hydrogen bonding interaction and form a slime. When viologen and AQS are dissolved inside the matrix, it becomes the solid state electrochromic slime. The solid state slime has a good flexibility that allows it to fold due to the soft nature of the matrix constructed through hydrogen bonding. Since Ag is electrochemically unstable and prone to oxidation incurring the loss of conductivity, it is not applicable to work as the counter electrode through a normal face-to-face device configuration. A lateral configuration is designed by placing a strand of electrochemically stable carbon fiber as the counter electrode surrounding the nanopaper working electrode. To complete the device, the electrochromic slime was spread across the working and counter electrode. The schematic for the device architecture is shown in **Figure 4a**.

As described above, the kinked Ag TCE is a high quality electrode with the Ag nanowires fusing at the junction. However, the Ag nanowires are not well protected against extraneous mechanical disturbance, e.g. the Ag nanowires become disconnected when the slime layer was peeled off (Figure S6a) while this problem is overcome by the SWCNT@Ag TCE with the SWCNT anchoring the Ag nanowire tightly to the nanopaper substrate even after peeling as seen in Figure S6 b and c. The kinked Ag nanowire is non-conductive in the peeled region while the SWCNT@Ag TCE demonstrates phenomenal stability by maintaining the high conductivity over 100 attach-and-peel cycles. (Figure S6d)

We studied the electrochromic performance of devices fabricated on kinked Ag and SWCNT@Ag through the folding test. The folding test is conducted at -180° for the whole

device with an optical modulation area of $1.5 \times 1.5 \text{ cm}^2$. The schematic for the folding test is shown in Figure S7. The electrochromic property is assessed at coloring and bleaching potential of -2 V and 0 V respectively. For the SWCNT@Ag device, an obvious contrast (ΔT) of 53.9% at 550 nm is achieved (Figure 4b). Since the Ag nanowires are anchored and protected by SWCNT, its contrast is well maintained with 96.3% retention after 20 folding cycles, and 70.1% retention even after 100 folding cycles as shown in Figure 4b. However, for the device based on kinked Ag nanowires, its contrast retention quickly drops to 43.9% after 20 folding cycles and 27.2% after 100 folding cycles (Figure 4c). The reason for such a major loss of optical modulation is due to the Ag nanowires delamination from the nanopaper substrate.

Studies on the dynamics of the electrochromic device have also been carried out. The switching time is defined as the time for attaining 90% optical modulation. The SWCNT@Ag based device delivers a fast switching with t_{coloring} and $t_{\text{bleaching}}$ of 11.5 s and 12.9 s respectively (Figure 4d). 20 folding cycles leave a negligible influence on the switching behavior with t_{coloring} and $t_{\text{bleaching}}$ of 11.8 s and 13.7 s. Even after 100 folding cycles, the switching time is only slightly increased to t_{coloring} and $t_{\text{bleaching}}$ of 13.6 s and 17.9 s respectively. The slightly sluggish kinetics should be due to the minor compromise of the electrode conductivity across the folding crease as discussed earlier. On the other hand, for the kinked Ag nanowire based device after folding, the switching behavior becomes inconsistent due to delamination of Ag and nonuniform coloration.

The coloration efficiency η is a factor that determines the readiness of one electrode to change color per unit coulomb/cm². A higher η indicates a lower power consumption to obtain a certain optical modulation. Coloration efficiency is defined in equation 3 below^[46]:

$$\eta = \Delta OD/q; \Delta OD = \log (T_{\text{bleach}}/T_{\text{color}}) \quad (3)$$

ΔOD indicates the change of optical density and q refers to charge transported to viologen per unit area. An excellent efficiency of $94.6 \text{ cm}^2/\text{C}$ is obtained for the foldable electrochromic device as shown in Figure 4e. This value is comparable to other reported viologen based devices^[1, 47, 48] considering the bulky polymer matrix that slows down the ion transportation compared to liquid electrolyte environment.^[49] The electrochromic device also demonstrates reasonably good cycling stability with contrast retention of 73.3% after 500 cycles and the device is still functioning with 31.7% retention even extensively cycled to 1500 cycles as shown in Figure 4f. Finally, a wearable camouflage device based on this foldable nanopaper was demonstrated. The whole device was flexed and mounted onto a bending wrist of around 65° bending angle (Figure 4g). The wearable device was displayed through an opening on a glove. Before coloring, the transparent device reveals the skin. A voltage of -2 V was then applied and drove the device to a red-purple color that hid the skin from vision and blended in with the color of the hand glove. The prototype camouflage device shows a working condition on skin under bending; depicting that futuristic wearable camouflage devices would be practicable with real-time multi-color electrochrome incorporated with matching absorption behavior to the surrounding.

3. Conclusion

In summary, kinked Ag nanowire TCE as well as the SWCNT@Ag TCE with excellent quality has been realized through a facile transfer method. SWCNTs not only bridge and fuse the Ag nanowires to enhance conductivity but also anchor and protect Ag nanowires from external deformation. A critical point was determined in which the bridging effect levels off. Subsequently, a transparent solid state foldable device based on the hybrid electrode was constructed. With this foldable electrochromic device of strong endurance to deformation,

excellent coloration efficiency and good cycling stability, we envision this as a good platform for the next generation deformable displays such as foldable e-screen and camouflage clothing.

4. Experimental Section

Nanopaper electrode fabrication: P3 typed SWCNT with surface carboxylic group purchased from Carbon Solutions was diluted in DI water to 1 wt%. The suspension was centrifuged at 10000 r/min for 5 mins for three times. 0.5 ml of the upper dispersed suspension was used and further diluted in 20 ml DI. Subsequently, 0.25 wt% surfactant Sodium dodecyl sulfate (SDS) was dissolved to further enhance the stability of the SWCNT suspension. The as-prepared SWCNT has a nominal concentration of 0.024 wt%. Ag nanowires (Seashell Technology, USA) with diameters of around 100 nm and an average length of 31.2 μm (Distribution in Figure S8) were diluted to 0.025 mg/ml in IPA. To form a double layered hybrid electrode, the nanopaper transfer method was used, namely, the SWCNT was filtered to form the first layer followed by the filtration of Ag nanowires. Then 0.5 g 0.1wt% TCNF (VTT) uniformly dispersed in 10 ml DI water was filtered to conformally cover the previously filtered conducting elements. Afterwards, the whole system was sandwiched between two glass slides and dried at 105 °C to assemble the nanofibers and facilitate the transfer process. Finally, the SWCNT@Ag nanopaper was peeled off from the filter membrane. The transfer mechanism utilizes the surface free energy difference between the filter membrane and nanocellulose, which has been described in our earlier publication based on PCNFs.^[5] The process for the fabrication of kinked Ag nanopaper electrode is the same to this procedure without the use of SWCNT.

Optimization of SWCNT amount: SWCNT with nominal concentration $c = 0.024$ wt% obtained is used. A Polydimethylsiloxane (PDMS) mask with an area $A=1.5\text{ cm} \times 1.5\text{ cm}$ was used for patterning. The amount for Ag nanowires was kept the same while SWCNT of different areal

density (D) was filtered. We define D of 1 ml SWCNT filtered as $D=1 \cdot c/A$; then areal densities of 0,0.25D,0.5D,0.75D and 1D were investigated. The obtained sheet resistance was correspondingly recorded against different amount of SWCNT filtered onto the same area A.

Fabrication of the foldable solid state electrochromic device: Electrochromic small molecule redox pairs of Ethyl Viologen Diperchlorate ($15 \text{ mmol} \cdot \text{L}^{-1}$) and Sodium Anthraquinone-2-sulfonate ($5 \text{ mmol} \cdot \text{L}^{-1}$) in combination with KCl ($20 \text{ mmol} \cdot \text{L}^{-1}$) were dissolved in 4 wt% PVA in DI solution. This was subsequently mixed with 4 wt% borax in DI solution in a volume ratio of 4:1 to form the hydrogen bonded slime. Conductive carbon fibers were weaved to form a strand which was settled laterally alongside the conducting electrode by double sided tapes. The electrochromic slime was then spread uniformly across the working and counter electrode.

Characterization: The morphology of nanocellulose and nanopaper electrode is investigated using Field Emission Scanning Electron Microscopy (FESEM) JEOL 7600F. The sample roughness is measured using an Atomic Force Microscope (AFM). Conductivity of the nanopaper electrode is evaluated by measuring the sheet resistance on a CMT-SR2000N four point probe. The diffusive transmittance is measured with an integrating sphere attachment in an UV-vis spectrophotometer (Shimadzu UV-3600). The electrochromic color switching was induced by polarizing the device between -2 V and 0 V with the voltage supply from Solartron 1470E.

Supporting Information

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

Acknowledgements

This work is supported by the Competitive Research Program (NRF-CRP13-2014-02) and NRF Investigatorship Award NRF-NRFI2015-05 under the National Research Foundation, Prime Minister's Office, Singapore. W. Kang acknowledges the scholarship awarded by Nanyang Technological University.

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Figure 1. FESEM images of a) TCNF nanofibril and b) a regular Kimwipes paper with large fiber diameters of 15-60 μm ; c) Digital image of a transparent TCNF nanopaper; d) Transmittance spectrum comparison between the TCNF nanopaper and glass slide; e) Fabrication procedure for the SWCNT@Ag TCE (inset shows a schematic of SWCNT anchoring Ag nanowire to the nanopaper substrate through hydrogen bonding between the carboxylic group of SWCNT and the hydroxyl group of nanocellulose).

Figure 2. a) FESEM image of the kinked Ag TCE with the red circles indicating the well fused junctions; FESEM images of the SWCNT@Ag TCE at b) low magnification and c) high magnification; Schematics showing the evolution of the kinked structure for Ag nanowire TCE with d) loosely packed out-of-plane nanowires after Ag filtration, e) conformal TCNF gel coverage after nanocellulose filtration, f) in-plane motion that leads to the kinked junction; g) sheet resistance as a function of SWCNT density under fixed Ag nanowire densities of M_1 and M_2 ; h) Transmittance spectra of kinked Ag TCEs and SWCNT@Ag TCEs at different sheet resistance; I) Comparison with selected important work on high quality TCEs. [5, 9, 13, 14, 26, 27, 36, 50, 51] [5,9,13,14,23,26,27,50,51]

Figure 3. a) Schematics for folding to different angles; b) Sheet resistance of the SWCNT@Ag electrode at different folding cycles; FESEM images of the SWCNT@Ag folded to c) -180° and d) 180°; Foldability test of SWCNT@Ag nanopaper electrode connected in a circuit with LED lights e) before and f) after crumpling.

Figure 4. a) The schematic of the electrochromic device configuration; Contrast of the electrochromic device based on b) SWCNT@Ag electrode and c) kinked Ag electrode at different folding cycles; d) Switching time of the SWCNT@Ag electrochromic device at different folding cycles; e) Coloration efficiency test of the SWCNT@Ag device; f) Cycling stability test; g) Demonstration of a camouflage device mounted on a bending wrist.

Table 1

	Sample 5	Sample 4	Sample 3	Sample 2	Sample 1
R_s for kinked Ag TCE (Ω/sq)	1.16	2.41	5.09	10.5	44.1
After Incorporation of SWCNT: R_s for SWCNT@Ag TCE (Ω/sq)	1.15	2.31	4.72	7.92	27.4
Improvement Factor	1.008	1.043	1.078	1.33	1.61
Kinked Ag TCE Transmittance	75.1	86.7	93.2	94.6	96.6
Kinked Ag TCE F.O.M	1055.6	1057.5	1033.3	637.8	245.0
SWCNT@Ag TCE Transmittance	73.9	84.3	89.8	90.9	92.7
SWCNT@Ag TCE F.O.M	1003.9	915.4	722.6	487.1	178.1

*Transmittance is taken at 600 nm with subtraction of the substrate.

Highly Transparent Conducting Nanopaper for Solid State Foldable Electrochromic Devices

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Figure S1. Surface roughness testing on AFM for a) TCNF nanopaper with RMS = 6.3 nm and b) PCNF with RMS = 65.6 nm.

Figure S2. a) Scatter angle measurement of the TCNF nanopaper; b) a digital clear and deep view through the transparent TCNF nanopaper; c) a digital hazy view of the PCNF nanopaper when lifted from the background.

The scatter angle is measured by projecting a laser point ($d=3$ mm) through the TCNF nanopaper surface, creating a scattered ring ($d=8.58$ mm) at a distance of 30 cm from the nanopaper plane. The calculated scatter angle is 1.06° , which is much smaller than that of PCNF with 21.6° [1].

This is reflected by a clear deep view through the TCNF nanopaper while the PCNF nanopaper is hazy even when lifted a short distance from the background.

Figure S3. a) FESEM image of the SWCNT@Ag TCE with SWCNT of 0.5D (the red circles indicate tightly packed Ag nanowire junctions); FESEM image of the SWCNT@Ag TCE with SWCNT of 1D where the close packing kinked structure is not observed.

Figure S4. FESEM images of the SWCNT@Ag TCE at different sheet resistance.

Figure S5. a) Cross section FESEM image of a TCNF nanopaper; b) Cross section FESEM image of a folded TCNF nanopaper.

Figure S6. a) FESEM image of the disolcated Ag nanowires for the kinked Ag TCE after slime peeling test; FESEM images for the SWCNT@Ag TCE after slime peeling test at b) low and c) high magnification.; d) variation of the sheet resistance against peeling cycles for the SWCNT@Ag TCE.

Figure S7. The shematic for the electrochromic device folding test at -180° (face to face). The folded crease is at the center.

Figure S8. Length distribution of the Ag nanowires adopted.

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