UC Berkeley

UC Berkeley Previously Published Works

Title

Fully R2R-Printed Carbon-Nanotube-Based Limitless Length of Flexible Active-Matrix for Electrophoretic Display Application

Permalink

<https://escholarship.org/uc/item/58n977cb>

Journal

Advanced Electronic Materials, 6(4)

ISSN

2199-160X

Authors

Sun, J
Sapkota, A
Park, H
et al.

Publication Date

2020-04-01

DOI

10.1002/aelm.201901431

Peer reviewed

Limitless-length, carbon nanotube-based, flexible TFT active matrix fabricated by an all roll-to-roll printing process

Junfeng Sun¹, Ashish Sapkota¹, Hyejin Park¹, Prince Wesley¹, Younsu Jung^{1,2}, Bijendra Bishow Maskey¹, Yushin Kim¹, Yutaka Majima², Jianfu Ding³, Jianying Ouyang³, Chang Guo³, Jacques Lefebvre³, Patrick. R. L. Malenfant³, Ali Javey^{4*} and Gyoujin Cho^{1*}

¹*Department of Printed Electronics Engineering, Sunchon National University,
Sunchon 540-742, Korea.*

²*Materials and Structure Laboratory, Tokyo Institute of Technology, Yokohama 226-
8503, Japan.*

³*National Research Council Canada M-50, 1200 Montreal Road, Ottawa, Ontario K1A
0R6, Canada.*

⁴*Electrical Engineering and Computer Sciences, University of California, Berkeley,
California 94720, United States.*

**E-mail: ajavey@berkeley.edu & gcho@sunchon.ac.kr.*

The theoretically limitless-length of a thin-film transistor (TFT) active matrix implies that virtually any surface can be rendered an interactive medium when laminated with electrophoretic or organic light-emitting diode sheets. However, performance, cost and size limitations of current fabrication technology and semiconducting materials typically utilized in TFT active matrices (TFT-AMs) have hindered progress, thus preventing the realization of a limitless-length TFT-AM. Herein, a high-purity semiconducting single-walled carbon nanotube (s-SWCNT) ink was formulated and employed in a fully additive manufacturing

process, in which roll-to-roll (R2R) gravure printing was used to fabricate a flexible TFT-AM to overcome the performance, cost and size limitations in fabricating a limitless-length TFT-AM with 10 to 40 PPI resolution (average mobility of $0.23 \pm 0.12 \text{ cm}^2/\text{Vs}$, average on-off ratio of $10^{4.1}$ and threshold voltage variation of $\pm 13\%$). As a proof of concept, an inexpensive and flexible e-paper display was demonstrated by simply laminating an electrophoretic sheet onto the R2R gravure-printed, s-SWCNT-based TFT-AM.

As the dawn of the ubiquitous computing draws near, the world is becoming more connected and integrated *via* the internet¹. This change has given the field of displays a preeminent role in communication and information exchange. As the leading mode of communication and information exchange, displays are becoming integrated into every part of daily life. This immersion of displays can be realized by manufacturing limitless-length flexible thin-film transistor active matrices (TFT-AMs) so that newspapers, signage, flyers, packages, apparel, wallpaper, etc. can be replaced by flexible displays, called the Display of Things (DoT). To fully realize the limitless-length of flexible display, however, flexible TFT-AMs should first be manufactured using a high-throughput and low-cost method, regardless of size, to drive down the price and allow market accessibility². Simply, the DoT indicates that all surfaces can become flexible displays that can be rolled and bent. In such case, the limitless-length of flexible display would revolutionize our surroundings by driving the development of a novel industries, through which myriads of new jobs would be created, akin to the Industrial Revolution. To achieve this practically, TFT-AMs, a core technology for displays, should be manufactured without cost and size limitations²⁻⁴. The solution can be found in roll-to-roll (R2R) additive manufacturing, such as R2R gravure printing, which has been used as a low-cost and limitless-length manufacturing technology for newspapers, magazines, packaging and wallpaper over the past 100 years⁵. If this technology can be adopted to manufacture TFT-AMs for displays, the limitless-length of flexible display

can be achieved by freely cut R2R laminated electrophoretic or organic light-emitting diode (OLED) sheets on R2R printed TFT-AMs (Fig. 1a).

However, none of the previously reported TFT-AMs fully printed^{6,7} or partially printed^{8,9} with semiconducting inks can be directly employed in display or signage because of the long curing times required for the inks^{10,11}, the prerequisite requirement of self-assembled monolayers¹², or the indispensable use of noble metals for drain/source electrodes to meet work function requirements¹³. Therefore, to attain a R2R-printed TFT-AMs with a comparable device yield and electrical performance to amorphous Si-based TFT-AMs, a rapidly curable (< 5 sec) semiconducting ink that yields a semiconducting thin film with an appropriate Fermi level to meet the work function of printed silver drain/source electrodes is required¹⁴. An adequate mobility and high on-off current ratio should be attained, where the printing speed is maintained above 6 m/min for all layers, including commercially available silver nanoparticle-based conducting ink and BaTiO₃ nanoparticle-based dielectric ink. Furthermore, a servo-mechanism with a high level of precision in the R2R printing system is required to simultaneously control overlay printing registration, web handling and ink transfer¹⁵. Unlike the R2R printing of media, the acceptable range for overlay printing registration accuracy (OPRA) during web transfer should be in the range of $\pm 20 \mu\text{m}$ ¹⁶ to print TFT-AMs with a maximum resolution of 40 PPI (pixel per inch). In addition, ink transfer from the printing roll to the mobile web should be well controlled, as the slightest variation in the amount of transferred ink usually causes a large variation in the threshold voltage (V_{th}) of the TFT-AM¹⁷. Therefore, to print TFT-AMs via the R2R method, ink transfer must be constant to avoid fluctuations in the turn-on voltage (V_{th}) and off current¹⁷. To remedy this problem, a R2R gravure system was developed to print TFT-AMs using a silver nanoparticle-based conducting ink and a BaTiO₃ nanoparticle-based dielectric ink with single-walled carbon nanotube (unsorted SWCNT containing 30% of metallic SWCNT)-based or poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-

80 b[thiophene] (PBTTT)-based semiconducting inks^{18,19}. This R2R gravure system was
 81 optimized with the aforementioned electronic inks to control the OPRA with an
 82 accuracy of ± 20 to $25\ \mu\text{m}$ at a printing speed of 6 to 12 m/min, resulting in a device
 83 yield of 95% or higher^{18,19}. However, despite these promising results, the
 84 aforementioned R2R gravure system cannot print TFT-AMs to operate displays due to
 85 the wide variation in V_{th} and low on-off current ratio (high off current) of TFT pixels in
 86 the printed TFT-AM. Both the V_{th} variation and low on-off current ratio preclude the
 87 selection of the desired TFT pixels, creating cross-talk between the pixels in the
 88 display²⁰. Therefore, for the R2R gravure-printed TFT-AM to properly operate an
 89 electrophoretic display, it needs to meet the minimum electrical characteristics required
 90 for the task²¹: $0.01\ \text{cm}^2/\text{Vs}$ mobility, $\pm 30\%$ variation in the V_{th} and 10^4 on-off current
 91 ratio. Presently, no reports have described an all R2R-printed TFT-AM that meets these
 92 minimum requirements for mobility, on-off current ratio and V_{th} variation while also
 93 overcoming both manufacturing cost and size limitations, because thus far no
 94 semiconductor ink has been reliable and robust enough to be employed in a R2R
 95 gravure printing system¹⁹. In this work, high-purity semiconducting SWCNTs (s-
 96 SWCNTs) were formulated as a gravure ink to meet these requirements and provide a
 97 drop-in solution utilizing our previously reported R2R gravure system^{18,19}. Other key
 98 specifications of the semiconducting ink include fast curing time ($< 5\ \text{sec}$), low curing
 99 temperature ($< 150\ ^\circ\text{C}$), ambient stability, consistent ink transfer from the engraved cell
 100 and wetting to the previously printed layer^{17,22}. By employing the high-purity s-
 101 SWCNT-based ink, the R2R gravure-printed s-SWCNT-based TFT-AM demonstrated
 102 promise for realizing the limitless-length of flexible display by printing both a low-
 103 resolution (10 PPI) and high-resolution (40 PPI) TFT-AMs with limitless length.
 104 Furthermore, the limitless-length of flexible display concept was demonstrated by
 105 utilizing a 20×20 s-SWCNT-based TFT-AM with 10 PPI resolution cut out from the
 106 printed roll and simply laminated with an electrophoretic sheet to create a flexible

107 electrophoretic display prototype that could easily be scaled for large-area signage (Fig.
108 1a).

109 **Pure s-SWCNT-based ink formulation**

110 To obtain the desired high-purity s-SWCNTs, a ligand exchange route was taken, in
111 which we first remove metallic SWCNTs using our previously reported extraction
112 process with poly(9,9-didodecylfluorene) (PFDD) to obtain a semiconducting purity of
113 99.9%, followed by ligand exchange with a polythiophene derivative (P3ME₄MT)^{23,24}.
114 This approach enables us to dial-in the desired s-SWCNT chirality distribution and high
115 semiconductor purity, as confirmed by absorption and Raman spectroscopy²⁵⁻²⁷.
116 Photoluminescence excitation (PLE) mapping confirms that the sorted s-SWCNTs
117 mainly comprise 9 chiralities, whereby the (10,9) chirality is predominant, with a
118 diameter of 1.30 nm (Supplementary Fig. S1a). The stronger interaction between the
119 nanotubes and polythiophenes compared to that with polyfluorenes facilitates the
120 exchange, which can be tracked during the process by spectral changes (Supplementary
121 Fig. S1b). The surface properties of the s-SWCNTs were tailored by wrapping s-
122 SWCNTs with P3ME₄MT (Supplementary Fig. S1c) for their dispersion in polar,
123 nontoxic solvent. P3ME₄MT possesses hydrophilic ω-methoxy tetraethoxy methyl side
124 chains, thus providing s-SWCNTs with good dispersibility in high-viscosity polar
125 solvents suitable for gravure printing, such as butyl carbitol and 1-octanol (Fig. 1a).
126 Optimized ink formulation (vide infra) provides adequate rheology for gravure printing
127 and wetting onto printed dielectric layers to enable TFT device fabrication with suitable
128 tube transfer without the need for rinsing. The sorted s-SWCNTs wrapped with
129 PME₄MT are obtained after two exchange cycles, after which most of the PFDD is
130 replaced, providing a composite that further enables fine tuning of the dispersibility of
131 the s-SWCNT material for ink formulation. The final product contains small amounts of
132 PFDD, with a PFDD/P3ME₄MT/CNT weight ratio of 0.4/2.0/1.0. As such, it can form
133 stable dispersions in 1-octanol. To the best of our knowledge, this approach has never

134 been exploited to formulate a functional s-SWCNT ink for printing. The amphiphilic
 135 polymer design (P3ME₄MT) enables ink formulation directly into 1-octanol, while
 136 minimizing excipient use compared to aqueous dispersions, and without using any other
 137 surfactant or binder to optimize ink transfer from the engraved cells on the gravure
 138 cylinder (for printing 20 × 20 TFT-AMs) to a poly(ethylene terephthalate) (PET) web at
 139 a web transfer speed of 6 m/min. The ink, with a surface tension of 30 mN/m and a
 140 viscosity of 11.7 cP, provided a good dispersion of s-SWCNTs (Supplementary Fig. S2).
 141 As formulated, this ink could be successfully transferred onto the printed dielectric layer
 142 at the aforementioned processing speed when the following conditions were met: 10°
 143 contact angle to the engraved gravure cell with 10 μm depth and 150 μm opening of the
 144 pyramidal structure (Supplementary Fig. S3). However, due to the different ink-transfer
 145 mechanism in printing high-resolution TFT-AMs with 40 PPI, the surface tension of the
 146 s-SWCNT ink was slightly altered by adding small amounts of toluene to the
 147 formulated s-SWCNT ink, which will be discussed in a later section of this paper.

148

149 **R2R gravure-printed TFT-AM with limitless length**

150 R2R gravure printing was performed following our previously reported method to
 151 fabricate a 20 × 20 TFT-AM with 10 PPI resolution (Fig. 1b). As shown in Fig. 1b to e,
 152 the R2R gravure-printed TFT-AM physically consists of gate electrodes (width of 330
 153 μm and thickness of 410 nm), pixel electrodes (1320 μm × 1580 μm × 410 nm),
 154 dielectric layers (width of 860 μm and thickness of 2.5 μm), SWCNT layers (35
 155 nanotubes/μm²) and drain/source electrodes (width of 1320 μm and thickness of 420
 156 nm) with a channel length of 60 μm. The physical dimensions are highly consistent
 157 along the whole length of the printed web (> 10 m). Due to the consistency of the
 158 physical structures in the R2R gravure-printed TFT-AM, the device yield was
 159 approximately 95% when characterized by selecting 13 TFT pixels per TFT-AM every
 160 2 m along the 10 m web (Fig. 2a and b). The device was characterized under ambient

161 conditions based on previously reported methods in which the effect of the quantum
 162 capacitance of the printed SWCNT network was negligible^{18,19}. The threshold voltage
 163 variation along 10 m of web was $\pm 6\%$ (Fig. 2c), with an average mobility of 0.03 ± 0.004
 164 cm^2/Vs (Fig. 2d) and average on-off current ratio of $10^{4.3 \pm 0.1}$ (Fig. 2e). Based on the
 165 electrical characteristics of the TFT-AM collected every 2 m along 10 m of web, the
 166 high-purity s-SWCNT-based ink provides a reliable and practical solution to
 167 manufacture a limitless length of TFT-AM. In addition, to prove the scalability of the
 168 R2R gravure system in terms of both size and resolution, a TFT-AM measuring 2.75×5
 169 in^2 with 40 PPI resolution was R2R printed under the same printing conditions.
 170 However, no working devices were observed, even with well-printed layers for gate
 171 electrodes, dielectric layers and drain/source electrodes (Supplementary Fig. S4),
 172 because the s-SWCNT ink was not properly transferred from the engraved gravure cell
 173 to the printed dielectric layer. In fact, the transfer of lower viscosity ink is more
 174 sensitive to variations in the cell structure than that of higher viscosity ink. The transfer
 175 of s-SWCNT-based ink was very poor due to the high surface tension of the ink on the
 176 shrunken gravure cell used to print the 40 PPI TFT-AM. Adding small amounts of
 177 toluene to the s-SWCNT ink reduced the surface tension, allowing good transfer from
 178 the gravure cell (Supplementary Fig. S5). Modifying the surface tension gave the s-
 179 SWCNT-based ink a similar viscosity to octanol-based ink, 11 cP, but with a lower
 180 surface tension of 28 mN/m (Supplementary Fig. S6). By employing the same R2R
 181 gravure system and the s-SWCNT ink with a slightly modified surface tension, a $76 \times$
 182 109 TFT-AM with 40 PPI was successfully R2R gravure printed, with a device yield of
 183 95%. The yield was determined by measuring 80 randomly selected TFT pixels per
 184 TFT-AM every 2 m along the 10 m PET web (Supplementary Fig. S7). The average
 185 mobility was $0.41 \pm 0.12 \text{ cm}^2/\text{V}$, with an average 20% variation in V_{th} and average on-off
 186 current of $10^{4.1}$. All device characteristics were similar to those of the 10 PPI TFT-AM,
 187 except for the one-order-higher mobility. The higher mobility results from the increased

ink-transfer rate using the shrunken gravure cell and shorter channel length²⁸. Based on the 10 PPI and 40 PPI TFT-AM results, a 40 PPI TFT-AM with a size of $2.75 \times$ limitless in^2 could be designed by simply connecting the beginning and end electrodes of the row lines in the TFT-AM on the gravure cylinder (Supplementary Fig. S8). With one rotation of this R2R gravure cylinder, a 15.7 in-long TFT-AM with 40 PPI was fabricated with a 95% device yield. When rotated 100 times, a 1,570 in-long TFT-AM with 40 PPI can be printed. An R2R-printed, 40 PPI TFT-AM produced from 5 rotations of the gravure cylinder, giving a size of $2.75 \times 78 \text{ in}^2$, was selected for characterization, and the measured average electrical characteristics, i.e., the mobility ($0.23 \pm 0.12 \text{ cm}^2/\text{Vs}$), average on-off current ratio ($10^{4.1}$) and average V_{th} variation (13%) (Fig. 2f), were comparable to those of the 76×109 TFT-AM with 40 PPI. From these results, we can directly speculate that the high-purity s-SWCNT-based R2R gravure system is indeed scalable for the fabrication of a limitless length of TFT-AM with low cost and consistent electrical properties. In other words, a 60 m-long, wall-sized display with a resolution of 40 PPI can be manufactured within 10 min via the R2R lamination of electrophoretic or OLED sheets on a R2R-printed TFT-AM.

R2R gravure-printed TFT-AM-based flexible electrophoretic display

To realize a R2R gravure-printed TFT-AM-based display, we selected a 20×20 TFT-AM with 10 PPI resolution due to the ease of construction of its driving IC. Before lamination of the electrophoretic sheet onto the 10 PPI TFT-AM, 400 TFT pixels should be characterized to understand the behavior of each TFT pixel in the TFT-AM. The results of the characterization of 400 TFTs among the randomly selected TFT-AM were almost identical to those obtained statistically along 10 m (Supplementary Fig. S9). However, during the characterization of all 400 TFTs in the TFT-AM under ambient conditions, a large variation in V_{th} was observed (Supplementary Fig. S9a) due to the long exposure to ambient conditions. The attained variation in V_{th} from 400 TFTs was

215 $\pm 24\%$ (Supplementary Fig. S9b), with an average mobility of $0.03 \pm 0.007 \text{ cm}^2/\text{Vs}$
 216 (Supplementary Fig. S9c) and average on-off current ratio of $10^{3.7 \pm 0.4}$ (Supplementary
 217 Fig. S9d). Because a narrow variation in V_{th} is necessary to properly operate the
 218 electrophoretic display, the large variation in V_{th} due to humidity should be minimized
 219 through a passivation process. However, because the V_{th} of a s-SWCNT-TFT is very
 220 sensitive to material contact, the shift in V_{th} must be minimized upon passivation.
 221 Among the previously reported materials used to passivate SWCNT-based TFTs, four
 222 different polymers (epoxy²⁹, poly(methylmethacrylate)³⁰, Cytop³¹ and
 223 poly(vinylphenol)/Polymethylsilsequioxane³²) were explored, and spin-coated Cytop
 224 showed the best passivation effect on our printed s-SWCNT-based TFT (Supplementary
 225 Fig. S10). After Cytop passivation, the R2R gravure-printed TFT-AM (400 TFTs) was
 226 characterized again (Fig. 3a and b). The V_{th} was stable with a variation of $\pm 5.6\%$ (Fig.
 227 3c) and maintained a similar mobility ($0.02 \pm 0.005 \text{ cm}^2/\text{Vs}$) (Fig. 3d) and on-off ratio
 228 ($10^{3.5 \pm 0.6}$) (Fig. 3e) to the non-passivated devices (Supplementary Fig. S9c and d). The
 229 variation in V_{th} garnered from the 400 TFTs is the best result among currently reported
 230 fully printed TFTs^{18,33} and can operate electrophoretic display pixels. Furthermore, the
 231 average on-off current ratio generated from the TFTs was enough to switch each pixel.
 232 A single transistor can switch a pixel with dimensions of $1320 \times 1580 \mu\text{m}^2$ because each
 233 transistor provides at least 600 nA of “on” current when the gate voltage is -20 V and
 234 the source voltage is -5 V. In addition, to avoid cross-talk with neighboring pixels, a
 235 single TFT in a series of pixels of the TFT-AM should not generate more than $\sim 10 \text{ nA}$
 236 of “off” current when a gate voltage of 0 V and drain/source voltage of -20 V or a gate
 237 voltage of -20 V and drain/source voltage of 0 V are applied (Supplementary Fig. S11).
 238 Based on the individual TFT characteristics, applying a voltage to a row (gate) (-20 V)
 239 and a column (source) (-5 V) of electrodes while maintaining a steady voltage (-15 V)
 240 turns on the pixel and provides a black color. To turn off the pixel (white color), the
 241 column was kept at -20 V and the row at -20 V while maintaining a steady voltage of -

15 V. To fully control 20×20 pixels, we employed a driving IC (Supplementary Fig. S12) to operate the electrophoretic display, with a switching speed of 0.3 Hz to ensure each pixel operated. However, the functional switching speed can be increased to 10 Hz in this driving IC system (see video file in the Supplementary Information to observe the speed of the pixel change in a row). Based on these operating conditions, the first fully R2R gravure-printed TFT-AM-based electrophoretic display was fabricated with a thickness of 0.4 mm (Fig. 4a) and operated by a custom made driving IC to display words, “RIC” and “PE” (Fig. 4b). An additional video in the Supplementary Information demonstrates the operation of the aforementioned flexible electrophoretic display based on our R2R gravure-printed TFT-AM.

Conclusions

Pure semiconducting SWCNTs (s-SWCNTs) with tailored surface properties using an amphiphilic polymer (P3ME₄MT) enabled the formulation of a gravure ink with octanol that meets the rheological properties and the surface tension required for the R2R gravure system to function at a printing speed of 6 m/min. Based on this novel ink and commercially available silver and BaTiO₃ inks, thin-film transistor active matrices (TFT-AMs) from low resolution (10 PPI) to high resolution (40 PPI) can be R2R printed, overcoming performance, cost and size limitations in fabricating TFT-AMs via a fully additive manufacturing process. As one of the preferred fully additive manufacturing processes, R2R gravure printing was used to fully print a TFT-AM with 10 PPI resolution at a printing speed of 6 m/min with a 96.5% device yield, an average mobility of $0.02 \pm 0.005 \text{ cm}^2/\text{Vs}$, average on-off current ratio of $10^{3.5 \pm 0.6}$, and a threshold voltage (V_{th}) variation of $\pm 5.6\%$ after passivation using Cytop. After lowering the surface tension of the s-SWCNT ink, this R2R gravure system was scaled to print a limitless length of TFT-AM with 40 PPI resolution. By selecting and characterizing a $2.75 \times 78 \text{ in}^2$ TFT-AM along 10 m of web, a consistent device yield (95%) with an

average mobility of $0.23 \pm 0.12 \text{ cm}^2/\text{Vs}$, average on-off current ratio of $10^{4.1}$, and a threshold voltage (V_{th}) variation of $\pm 13\%$ was attained. Because this R2R gravure system demonstrated 95% device yield with consistent electrical properties along the entire length of the 10 m PET web with no limitation in the resolution up to 40 PPI, the flexible and rollable TFT-AM could be easily scaled to a limitless length with low cost. This R2R gravure system utilizing high-purity s-SWCNT ink will be a core technology to make the DoT a reality. To demonstrate the validity of using R2R-printed TFT-AMs for the DoT, the concept was demonstrated by simply laminating an electrophoretic sheet on the R2R gravure-printed s-SWCNT-based TFT-AM with 10 PPI. Furthermore, the insights obtained herein suggest that the R2R gravure-printed TFT-AM can be extended to operate OLED displays by improving the mobility of TFTs up to $5 \text{ cm}^2/\text{Vs}^{34}$ while keeping the presently attained threshold voltage variation ($\pm 5\%$). Thus, the results reported above are the first steps in realizing the DoT and can be directly utilized in current packaging and large-area flexible signage technology.

283

284 **Methods**

285 Materials. The silver nanoparticle-based ink used to print gates, contact electrodes and drain/source electrodes was purchased from PARU (PG-007), and its viscosity was adjusted to 1000 cP to print the gate and contact electrodes, while a viscosity of 1200 cP was used to print the drain/source electrodes. BaTiO₃ nanoparticle-based dielectric ink was also purchased from PARU (PD-100) and used without any further dilution. s-SWCNTs were prepared using a reported PFDD extraction process using plasma SWCNTs and a PFDD/CNT ratio of 1.25/1.00. Then, 300 mg of this sample was added with 300 mg of P3ME₄MT in 1000 ml of toluene. The mixture was bath sonicated for 30 min to completely disperse the SWCNTs and form a homogeneous solution, which was then filtered through a Teflon membrane with a pore size of 0.2 μm (Sartorius Stedim Biotech GmbH) to collect the SWCNTs. The obtained film was soaked in

296 toluene to remove free polymer. This exchange step was repeated once more using 750
297 mg of PME_4MT to obtain the final sample, which was dried before formulation as a
298 semiconducting ink using 1-octanol (Junsei Chemical Co., Ltd., Japan). The sorted
299 SWCNTs (15 mg) were dispersed in 1-octanol (30 mL) using probe sonication for 3 hrs.
300 The resulting ink provided a stable dispersion of s-SWCNTs, and its stability was
301 characterized by UV-NIR spectroscopy (JASCO V-670). Furthermore, its rheological
302 characteristics were studied using a HAAKE MARS modular advanced rheometer
303 system at 25 °C.

304 **TFT-AM fabrication using R2R gravure printing.** In general, the R2R gravure
305 printing method was the same as previously reported.¹⁷ First, gate electrodes and contact
306 electrodes were printed at a speed of 6 m/min using silver nanoparticle-based ink. Then,
307 the dielectric layers were printed at the same speed using BaTiO_3 nanoparticle-based
308 ink. The resulting printed PET web was rewound to print the s-SWCNTs at the same
309 speed. After printing the s-SWCNTs, the web was rewound again to print drain/source
310 electrodes and wires at the same speed. The resulting s-SWCNT-based TFT-AMs with
311 resolutions of 10 PPI and 40 PPI were characterized by selecting one TFT-AM every 2
312 m along 10 m of PET web. To demonstrate the limitless length of 40 PPI TFT-AM
313 fabrication, 78 in of TFT-AM, printed by 5 rotations of the gravure cylinder, was
314 selected along the length of the 10 m web to characterize the device yield with electrical
315 properties.

316 **Laminating e-ink on the R2R gravure-printed TFT-AM.** For the operational
317 demonstration of e-paper using the R2R gravure-printed TFT-AM, the e-ink was
318 laminated on the TFT-AM via exposed contact electrodes in the TFT-AM, where TFTs
319 were passivated by first screen printing vacuum grease only on the contact electrodes.
320 Cytop (Asahi Glass Co., Japan) was then spin coated. After spin coating, the printed

vacuum grease was washed away by hexane to selectively expose the contact electrodes to contact the bottom electrodes of the electrophoretic sheet (Fig. 4a).

TFT characterization. The transfer, output and leakage characteristics of TFTs in the active matrix were measured using a KEITHLEY 4200 Semiconductor Characterization System (USA) with an ambient probe station (MS TECH(MST-4000A)). All attained data were analyzed using a custom Origin script to obtain the mobility, threshold voltage and on-off current ratio.

Electrophoretic display demonstration. The e-paper demonstration was carried out using a custom-made controller that employed the row-to-row scanning (gate line) method. The microcontroller (ATmega2560) used in this driving IC could only supply voltage in the range 0-5 V. Therefore, to drive the R2R gravure-printed TFT-AM-based e-paper, a higher voltage (-20 V to +20 V) was needed. To provide enough voltage, a level shifter circuit was designed by using Opamp (LT1491) to convert the low digital output voltage (0-5 V) to higher voltage (-20 V to +20 V). To show a particular image on the e-paper, the e-paper was first turned to the white (clear) state ($V_{\text{comm}}=+20$ V, $V_g=-20$ V, $V_s=-20$ V). After V_{comm} was set to -15 V, the gate lines were scanned one by one (the voltage of the gate scan lines was -20 V, while the other scan lines had a voltage of +20 V). The source lines were set to the desired value (ON: V_s of -5 V and OFF: V_s of -20 V) to control the e-paper pixels. To control the contrast of the e-paper, the V_{comm} potential was increased from -10V to -15 V as the pixels became darker due to the increase in the potential difference between the top and bottom electrodes of the e-paper. The scanning rate of the gate lines also affected the contrast of the display. At a scanning speed greater than 0.5 Hz, the pixels did not work properly, so the threshold scanning speed was set to approximately 0.3 Hz.

345 **Acknowledgements** The authors thank the Ministry of Education in Korea for financial
 346 support through the Basic Science Research Program in Sunchon National University
 347 (NRF-2014R1A6A1030419) and the Global Leading Technology Program of the Office
 348 of Strategic R&D Planning (OSP), funded by the Ministry of Commerce, Industry and
 349 Energy, Republic of Korea (10042537, Printed Electronics Total Solution
 350 Development).

351 **Author contributions** G.C. and A.J. conceived and designed the experiments. J.S.
 352 conducted the experiments. A.S. designed and set up the e-paper operation IC system
 353 and carried out the final electrophoretic display operation. J.S., H.P. and Y.J. carried out
 354 the ink formulation, printing experiments and device characterization. P.W. simulated s-
 355 SWCNT ink transfer. J.D., J.O., C.G., J.L. and P.R.L.M. designed, prepared and
 356 analyzed the s-SWCNTs. Y.M. provided and analyzed the SEM information. G.C.
 357 wrote the paper, and all authors provided feedback.

358 **References**

- 359 1. Ning, H. Unit and ubiquitous internet of things. Ch. 1 (CRC Press, Taylor &
 360 France Group, Boca Raton, 2013).
- 361 2. Chen, P. *et al.* Fully printed separated carbon nanotube thin film transistor
 362 circuits and its application in organic light emitting diode control. *Nano Lett.* **11**,
 363 5301-5308 (2011).
- 364 3. Goh, J. C., Chung, H. J., & Han, C. H. A new pixel circuit for active matrix
 365 organic light emitting diodes. *IEEE Electron Device Lett.*, **23**, 544-546 (2002).

- 366 4. Shirasaki, T, *et al.* Full-color polymer AM-OLED using ink-jet and a-Si TFT
367 technologies. *SID Tech. Dig.* 1516-1517 (2004).
- 368 5. Lilien, O. M. History of industrial gravure printing up to 1920. 45–54 (Lund
369 Humphries Publishers Ltd, London, 1972).
- 370 6. Jung, M. *et al.* All-printed and roll-to-roll printable 13.56-MHz-operated 1-bit
371 RF tag on plastic foils. *IEEE Trans. Electron Device.* **57**, 571-580 (2010).
- 372 7. Lau, P. *et al.* Fully printed, high performance carbon nanotube thin-film
373 transistors on flexible substrates. *Nano Lett.* **13**, 3864-3869 (2013).
- 374 8. Kawase, T. *et al.* Inkjet printing of polymer thin film transistors. *Thin Solid*
375 *Films* **438-439**, 279-287 (2003).
- 376 9. Yan, H. *et al.* A high-mobility electron-transporting polymer for printed
377 transistors. *Nature* **457**, 679-865 (2009).
- 378 10. Shin, K. *et al.* Roll-to-roll gravure printing of thick-film silver electrode
379 micropatterns for flexible printed circuit board. *J. Coat. Technol. Res.*, **14** (1)
380 95-106 (2017).
- 381 11. Leppamiemi, J. *et al.* Rapid low-temperature processing of metal-oxide thin
382 film
383 transistors with combined far ultraviolet and thermal annealing. *Appl. Phys.Lett.*
384 **105**. 113514 (2014).
- 385 12. Nakano, M. *et al.* Control of major carriers in an ambipolar polymer
386 semiconductor by self-assembled monolayers. *Adv, Mater.* **29**.1602893 (2017).

- 387 13. Haratipour, N. *et al.* Fundamental limits on the subthreshold slope in schottky
388 source/drain black phosphorus field-effect transistors. *ACS Nano* **10**, 3791-3800
389 (2016).
- 390 14. Kim, T. *et al.* Electrical properties of synthesized large-area MoS₂ field-effect
391 transistors fabricated with inkjet-printed contacts. *ACS Nano*. **10**, 2819-2826
392 (2016).
- 393 15. Koo, H. *et al.* Scalability of carbon-nanotube based thin film transistors for
394 flexible electronic devices manufactured using an all roll-to-roll gravure
395 printing system. *Sci. Rep.* **5**, 14459; doi:10.1038/srep14459 (2015).
- 396 16. Lee, J. *et al.* Register control algorithm for high resolution multilayer printing in
397 the roll-to-roll process. *MSSP*. **60-61**, 706-714 (2015).
- 398 17. Noh, J. *et al.* Key issues with printed flexible thin film transistors and their
399 application in disposable RF sensors. *Proc. IEEE*. **103**, 554–566 (2015).
- 400 18. Lee, W. *et al.* A fully roll-to-roll gravure-printed carbon nanotube-based active
401 matrix for multi-touch sensors. *Sci. Rep.* **5**, 17707; doi: 10.1038/srep17707
402 (2015).
- 403 19. Sun, J. *et al.* Proving scalability of an organic semiconductor to print a TFT
404 active *matrix* using a roll-to-roll gravure. *ACS Omega* **2**, 5766-5774 (2017).
- 405 20. Cao, X. *et al.* Fully screen-printed, large-area, and flexible active-matrix
406 electrochromic displays using carbon nanotube thin-film transistors. *ACS Nano*
407 **10**, 9816-9822 (2016).

- 408 21. Gelinck, G., Heremans, P., Nomoto, K., & Anthopoulos, T. D. Organic
409 transistors in optical displays and microelectronic applications. *Adv. Mat.* **22**,
410 3778-3798 (2010).
- 411 22. Kopola, P. *et al.* Gravure printed organic light emitting diodes for lighting
412 applications. *Thin Solid Films* **517**, 5757-5762 (2009).
- 413 23. Stranks, S. D., Baker, A. M. R., Alexander-Webber, J. A., Dirks, B. &
414 Nicholas, R. J. Production of high-purity single-chirality carbon nanotube
415 hybrids by selective polymer exchange. *Small* **9**, 2245–2249, (2013).
- 416 24. Stranks, S. D., Habisreutinger, S. N., Dirks, B., & Nicholas, R. J. Novel carbon
417 nanotube-conjugated polymer nanohybrids produced by multiple polymer
418 processing. *Adv. Mater.* **25**, 4365–4371, (2013).
- 419 25. Ding, J. *et al.* Enrichment of large-diameter semiconducting SWCNTs by
420 polyfluorene extraction for high network density thin film transistors.
421 *Nanoscale* **6**, 2328–2339, (2014).
- 422 26. Ding, J. *et al.* A hybrid enrichment process combining conjugated polymer
423 extraction and silica gel adsorption for high purity semiconducting single-
424 walled carbon nanotubes (SWCNT). *Nanoscale* **7**, 15741–15747, (2015).
- 425 27. Li, Z. *et al.* Raman microscopy mapping for the purity assessment of chirality
426 enriched carbon nanotube networks in thin-film transistors. *Nano Research.* **8**,
427 2179–2187. (2015).
- 428 28. Sirringhaus, H. *et al.* High-Resolution Inkjet Printing of All-polymer Transistor
429 Circuits. *Science* **290**, 2123-2126 (2000).

- 430 29. Kim, D. *et al.* Fully Gravure Printed Complementary Carbon Nanotube TFTs
431 for Clock Signal Generator Using Epoxy-Imine Based Cross-linker as n-Dopant
432 and Encapsulant. *Nanoscale* **47**.19876-19881 (2016).
- 433 30. Yang, Y. *et al.* Low Hysteresis Carbon Nanotube Transistors Constructed via a
434 General Dry-Laminating Encapsulation Method on Diverse Surfaces. *ACS Appl.*
435 *Mater. Interfaces*. **9**.14292-14300 (2017).
- 436 31. Ha, T. *et al.* Highly Stable Hysteresis-Free Carbon Nanotube Thin-Film
437 Transistors by Fluorocarbon Polymer Encapsulation. *ACS Appl. Mater.*
438 *Interfaces*. **6**. 8441-8446 (2014).
- 439 32. Homenick, C. *et al.* Fully Printed and Encapsulated SWCNT-Based Thin Film
440 Transistors via a Combination of R2R Gravure and Inkjet Printing. *ACS Appl.*
441 *Mater. Interfaces*. **8**. 27900-27910 (2016).
- 442 33. Yeom, C. *et al.* Large-area compliant tactile sensors using printed carbon
443 nanotube active-matrix backplanes. *Adv. Mat.* **27**. 1561-1566 (2015).
- 444 34. Lefebvre, J, J. *et al.* High-purity semiconducting single-walled carbon
445 nanotubes: a key enabling material in emerging electronics. *Acc. Chem. Res.*, **50**.
446 2479-2486 (2017).

447

448

449

450

451 **Figure legends**

452 **Figure 1.** Concept image of fabricating signage by simply laminating OLED or
 453 electrophoretic sheets on R2R gravure printed TFT-active matrix and then, cut and paste
 454 the signage on a plastic container (a). Roll of R2R gravure printed TFT-active matrix
 455 with 10 PPI resolutions (b) and one selected TFT-active matrix (c). Optical images of
 456 12 pixels (d), and a cross-sectional FIB-SEM image with the inset of printed s-
 457 SWCNTs on printed dielectric layer (e).

458 **Figure 2.** Optical image of R2R gravure printed 10 PPI TFT-active matrix along 10 m
 459 PET roll (a). The transfer characteristics of 50 TFTs randomly attained every 10 TFTs
 460 per 2 m along 10 m long of printed PET web (b) with statistical data of extracted
 461 threshold voltage (V_{th}) (c), mobility (d), and on-off current ratio (e). Optical image of
 462 R2R gravure printed 40 PPI TFT-active matrix without the length limit and the attained
 463 transfer characteristics by randomly measured 80 TFTs per randomly selected 15.7 inch
 464 length (f).

465 **Figure 3.** The TFT-active matrix image (a) characteristics of TFTs attained from 400
 466 TFTs in a 20×20 printed TFT-AM after passivated with Cytop (b). The statistical data
 467 of extracted threshold voltage (V_{th}) (c), mobility (d), and on-off current ratio (e).

468

469 **Figure 4** The selected TFT-active matrix was passivated after masked pixel electrodes
 470 by vacuum grease (a) and then, washed off the vacuum grease to reveal the electrodes
 471 again to contact the bottom electrodes of the e-paper by laminating e-ink. The resulting
 472 e-paper was operated by custom made driving IC system to show words such as “RIC”
 473 and “PE”.

474