Title

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

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

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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±0.12 cm^2/Vs, average on-off ratio of $10^{4.1}$ and threshold voltage variation of ±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 internet[1]. 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 accessibility[2]. 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 limitations[2-4]. 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 years[5]. 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 monolayers[12], or the indispensable use of noble metals for drain/source electrodes to meet work function requirements[13]. 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 required[14]. 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 $BaTiO_3$ 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 transfer[15]. Unlike the R2R printing of media, the acceptable range for overlay printing registration accuracy (OPRA) during web transfer should be in the range of ±20 μm[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-AM[17]. 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 current[17]. To remedy this problem, a R2R gravure system was developed to print TFT-AMs using a silver nanoparticle-based conducting ink and a $BaTiO_3$ 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-

b]thiophene] (PBTTT)-based semiconducting inks[18,19]. This R2R gravure system was optimized with the aforementioned electronic inks to control the OPRA with an accuracy of ±20 to 25 μm at a printing speed of 6 to 12 m/min, resulting in a device yield of 95% or higher[18,19]. However, despite these promising results, the aforementioned R2R gravure system cannot print TFT-AMs to operate displays due to the wide variation in V_{th} and low on-off current ratio (high off current) of TFT pixels in the printed TFT-AM. Both the V_{th} variation and low on-off current ratio preclude the selection of the desired TFT pixels, creating cross-talk between the pixels in the display[20]. Therefore, for the R2R gravure-printed TFT-AM to properly operate an electrophoretic display, it needs to meet the minimum electrical characteristics required for the task[21]: 0.01 cm^2/Vs mobility, ±30% variation in the V_{th} and 10^4 on-off current ratio. Presently, no reports have described an all R2R-printed TFT-AM that meets these minimum requirements for mobility, on-off current ratio and V_{th} variation while also overcoming both manufacturing cost and size limitations, because thus far no semiconductor ink has been reliable and robust enough to be employed in a R2R gravure printing system[19]. In this work, high-purity semiconducting SWCNTs (s-SWCNTs) were formulated as a gravure ink to meet these requirements and provide a drop-in solution utilizing our previously reported R2R gravure system[18,19]. Other key specifications of the semiconducting ink include fast curing time (<5 sec), low curing temperature (< 150 °C), ambient stability, consistent ink transfer from the engraved cell and wetting to the previously printed layer[17,22]. By employing the high-purity s-SWCNT-based ink, the R2R gravure-printed s-SWCNT-based TFT-AM demonstrated promise for realizing the limitless-length of flexible display by printing both a low-resolution (10 PPI) and high-resolution (40 PPI) TFT-AMs with limitless length. Furthermore, the limitless-length of flexible display concept was demonstrated by utilizing a 20 × 20 s-SWCNT-based TFT-AM with 10 PPI resolution cut out from the printed roll and simply laminated with an electrophoretic sheet to create a flexible

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

Pure s-SWCNT-based ink formulation

To obtain the desired high-purity s-SWCNTs, a ligand exchange route was taken, in which we first remove metallic SWCNTs using our previously reported extraction process with poly(9,9-didodecylfluorene) (PFDD) to obtain a semiconducting purity of 99.9%, followed by ligand exchange with a polythiophene derivative ($P3ME_4MT$)[23,24]. This approach enables us to dial-in the desired s-SWCNT chirality distribution and high semiconductor purity, as confirmed by absorption and Raman spectroscopy[25-27]. Photoluminescence excitation (PLE) mapping confirms that the sorted s-SWCNTs mainly comprise 9 chiralities, whereby the (10,9) chirality is predominant, with a diameter of 1.30 nm (Supplementary Fig. S1a). The stronger interaction between the nanotubes and polythiophenes compared to that with polyfluorenes facilitates the exchange, which can be tracked during the process by spectral changes (Supplementary Fig. S1b). The surface properties of the s-SWCNTs were tailored by wrapping s-SWCNTs with $P3ME_4MT$ (Supplementary Fig. S1c) for their dispersion in polar, nontoxic solvent. $P3ME_4MT$ possesses hydrophilic ω-methoxy tetraethoxy methyl side chains, thus providing s-SWCNTs with good dispersibility in high-viscosity polar solvents suitable for gravure printing, such as butyl carbitol and 1-octanol (Fig. 1a). Optimized ink formulation (vide infra) provides adequate rheology for gravure printing and wetting onto printed dielectric layers to enable TFT device fabrication with suitable tube transfer without the need for rinsing. The sorted s-SWCNTs wrapped with PME_4MT are obtained after two exchange cycles, after which most of the PFDD is replaced, providing a composite that further enables fine tuning of the dispersibility of the s-SWCNT material for ink formulation. The final product contains small amounts of PFDD, with a PFDD/$P3ME_4MT$/CNT weight ratio of 0.4/2.0/1.0. As such, it can form stable dispersions in 1-octanol. To the best of our knowledge, this approach has never

been exploited to formulate a functional s-SWCNT ink for printing. The amphiphilic polymer design ($P3ME_4MT$) enables ink formulation directly into 1-octanol, while minimizing excipient use compared to aqueous dispersions, and without using any other surfactant or binder to optimize ink transfer from the engraved cells on the gravure cylinder (for printing 20 × 20 TFT-AMs) to a poly(ethylene terephthalate) (PET) web at a web transfer speed of 6 m/min. The ink, with a surface tension of 30 mN/m and a viscosity of 11.7 cP, provided a good dispersion of s-SWCNTs (Supplementary Fig. S2). As formulated, this ink could be successfully transferred onto the printed dielectric layer at the aforementioned processing speed when the following conditions were met: 10° contact angle to the engraved gravure cell with 10 μm depth and 150 μm opening of the pyramidal structure (Supplementary Fig. S3). However, due to the different ink-transfer mechanism in printing high-resolution TFT-AMs with 40 PPI, the surface tension of the s-SWCNT ink was slightly altered by adding small amounts of toluene to the formulated s-SWCNT ink, which will be discussed in a later section of this paper.

R2R gravure-printed TFT-AM with limitless length

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

conditions based on previously reported methods in which the effect of the quantum capacitance of the printed SWCNT network was negligible[18,19]. The threshold voltage variation along 10 m of web was ±6% (Fig. 2c), with an average mobility of 0.03±0.004 cm^2/Vs (Fig. 2d) and average on-off current ratio of $10^{4.3\pm0.1}$ (Fig. 2e). Based on the electrical characteristics of the TFT-AM collected every 2 m along 10 m of web, the high-purity s-SWCNT-based ink provides a reliable and practical solution to manufacture a limitless length of TFT-AM. In addition, to prove the scalability of the R2R gravure system in terms of both size and resolution, a TFT-AM measuring 2.75 × 5 in^2 with 40 PPI resolution was R2R printed under the same printing conditions. However, no working devices were observed, even with well-printed layers for gate electrodes, dielectric layers and drain/source electrodes (Supplementary Fig. S4), because the s-SWCNT ink was not properly transferred from the engraved gravure cell to the printed dielectric layer. In fact, the transfer of lower viscosity ink is more sensitive to variations in the cell structure than that of higher viscosity ink. The transfer of s-SWCNT-based ink was very poor due to the high surface tension of the ink on the shrunken gravure cell used to print the 40 PPI TFT-AM. Adding small amounts of toluene to the s-SWCNT ink reduced the surface tension, allowing good transfer from the gravure cell (Supplementary Fig. S5). Modifying the surface tension gave the s-SWCNT-based ink a similar viscosity to octanol-based ink, 11 cP, but with a lower surface tension of 28 mN/m (Supplementary Fig. S6). By employing the same R2R gravure system and the s-SWCNT ink with a slightly modified surface tension, a 76 × 109 TFT-AM with 40 PPI was successfully R2R gravure printed, with a device yield of 95%. The yield was determined by measuring 80 randomly selected TFT pixels per TFT-AM every 2 m along the 10 m PET web (Supplementary Fig. S7). The average mobility was 0.41±0.12 cm^2/V, with an average 20% variation in V_{th} and average on-off current of $10^{4.1}$. All device characteristics were similar to those of the 10 PPI TFT-AM, except for the one-order-higher mobility. The higher mobility results from the increased

188 ink-transfer rate using the shrunken gravure cell and shorter channel length[28]. Based on
189 the 10 PPI and 40 PPI TFT-AM results, a 40 PPI TFT-AM with a size of 2.75 ×
190 limitless in^2 could be designed by simply connecting the beginning and end electrodes
191 of the row lines in the TFT-AM on the gravure cylinder (Supplementary Fig. S8). With
192 one rotation of this R2R gravure cylinder, a 15.7 in-long TFT-AM with 40 PPI was
193 fabricated with a 95% device yield. When rotated 100 times, a 1,570 in-long TFT-AM
194 with 40 PPI can be printed. An R2R-printed, 40 PPI TFT-AM produced from 5
195 rotations of the gravure cylinder, giving a size of 2.75 × 78 in^2, was selected for
196 characterization, and the measured average electrical characteristics, i.e., the mobility
197 (0.23±0.12 cm^2/Vs), average on-off current ratio ($10^{4.1}$) and average V_{th} variation (13%)
198 (Fig. 2f), were comparable to those of the 76 × 109 TFT-AM with 40 PPI. From these
199 results, we can directly speculate that the high-purity s-SWCNT-based R2R gravure
200 system is indeed scalable for the fabrication of a limitless length of TFT-AM with low
201 cost and consistent electrical properties. In other words, a 60 m-long, wall-sized display
202 with a resolution of 40 PPI can be manufactured within 10 min via the R2R lamination
203 of electrophoretic or OLED sheets on a R2R-printed TFT-AM.
204
205 **R2R gravure-printed TFT-AM-based flexible electrophoretic display**
206 To realize a R2R gravure-printed TFT-AM-based display, we selected a 20 × 20 TFT-
207 AM with 10 PPI resolution due to the ease of construction of its driving IC. Before
208 lamination of the electrophoretic sheet onto the 10 PPI TFT-AM, 400 TFT pixels should
209 be characterized to understand the behavior of each TFT pixel in the TFT-AM. The
210 results of the characterization of 400 TFTs among the randomly selected TFT-AM were
211 almost identical to those obtained statistically along 10 m (Supplementary Fig. S9).
212 However, during the characterization of all 400 TFTs in the TFT-AM under ambient
213 conditions, a large variation in V_{th} was observed (Supplementary Fig. S9a) due to the
214 long exposure to ambient conditions. The attained variation in V_{th} from 400 TFTs was

±24% (Supplementary Fig. S9b), with an average mobility of 0.03±0.007 cm^2/Vs (Supplementary Fig. S9c) and average on-off current ratio of $10^{3.7\pm0.4}$ (Supplementary Fig. S9d). Because a narrow variation in V_{th} is necessary to properly operate the electrophoretic display, the large variation in V_{th} due to humidity should be minimized through a passivation process. However, because the V_{th} of a s-SWCNT-TFT is very sensitive to material contact, the shift in V_{th} must be minimized upon passivation. Among the previously reported materials used to passivate SWCNT-based TFTs, four different polymers (epoxy[29], poly(methylmethacrylate)[30], Cytop[31] and poly(vinylphenol)/Polymethylsilsesquioxane[32]) were explored, and spin-coated Cytop showed the best passivation effect on our printed s-SWCNT-based TFT (Supplementary Fig. S10). After Cytop passivation, the R2R gravure-printed TFT-AM (400 TFTs) was characterized again (Fig. 3a and b). The V_{th} was stable with a variation of ±5.6% (Fig. 3c) and maintained a similar mobility (0.02±0.005 cm^2/Vs) (Fig. 3d) and on-off ratio ($10^{3.5\pm0.6}$) (Fig. 3e) to the non-passivated devices (Supplementary Fig. S9c and d). The variation in V_{th} garnered from the 400 TFTs is the best result among currently reported fully printed TFTs[18,33] and can operate electrophoretic display pixels. Furthermore, the average on-off current ratio generated from the TFTs was enough to switch each pixel. A single transistor can switch a pixel with dimensions of 1320 × 1580 μm^2 because each transistor provides at least 600 nA of "on" current when the gate voltage is - 20 V and the source voltage is -5 V. In addition, to avoid cross-talk with neighboring pixels, a single TFT in a series of pixels of the TFT-AM should not generate more than ~10 nA of "off" current when a gate voltage of 0 V and drain/source voltage of -20 V or a gate voltage of -20 V and drain/source voltage of 0 V are applied (Supplementary Fig. S11). Based on the individual TFT characteristics, applying a voltage to a row (gate) (-20 V) and a column (source) (-5 V) of electrodes while maintaining a steady voltage (-15 V) turns on the pixel and provides a black color. To turn off the pixel (white color), the 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 (P3ME$_4$MT) 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 $BaTiO_3$ 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±0.005 cm^2/Vs, average on-off current ratio of $10^{3.5\pm0.6}$, and a threshold voltage (V_{th}) variation of ±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 × 78 in^2 TFT-AM along 10 m of web, a consistent device yield (95%) with an

269 average mobility of 0.23±0.12 cm^2/Vs, average on-off current ratio of $10^{4.1}$, and a
270 threshold voltage (V_{th}) variation of ±13% was attained. Because this R2R gravure
271 system demonstrated 95% device yield with consistent electrical properties along the
272 entire length of the 10 m PET web with no limitation in the resolution up to 40 PPI, the
273 flexible and rollable TFT-AM could be easily scaled to a limitless length with low cost.
274 This R2R gravure system utilizing high-purity s-SWCNT ink will be a core technology
275 to make the DoT a reality. To demonstrate the validity of using R2R-printed TFT-AMs
276 for the DoT, the concept was demonstrated by simply laminating an electrophoretic
277 sheet on the R2R gravure-printed s-SWCNT-based TFT-AM with 10 PPI. Furthermore,
278 the insights obtained herein suggest that the R2R gravure-printed TFT-AM can be
279 extended to operate OLED displays by improving the mobility of TFTs up to 5
280 cm^2/Vs[34] while keeping the presently attained threshold voltage variation (±5%). Thus,
281 the results reported above are the first steps in realizing the DoT and can be directly
282 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
286 drain/source electrodes was purchased from PARU (PG-007), and its viscosity was
287 adjusted to 1000 cP to print the gate and contact electrodes, while a viscosity of 1200 cP
288 was used to print the drain/source electrodes. $BaTiO_3$ nanoparticle-based dielectric ink
289 was also purchased from PARU (PD-100) and used without any further dilution. s-
290 SWCNTs were prepared using a reported PFDD extraction process using plasma
291 SWCNTs and a PFDD/CNT ratio of 1.25/1.00. Then, 300 mg of this sample was added
292 with 300 mg of $P3ME_4MT$ in 1000 ml of toluene. The mixture was bath sonicated for
293 30 min to completely disperse the SWCNTs and form a homogeneous solution, which
294 was then filtered through a Teflon membrane with a pore size of 0.2 μm (Sartorius
295 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_{comm}=+20 V, Vg=-20 V, Vs=-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: Vs of -5 V and OFF: Vs 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.

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

References

1. Ning, H. Unit and ubiquitous internet of things. Ch. 1 (CRC Press, Taylor & France Group, Boca Raton, 2013).

2. Chen, P. *et al.* Fully printed separated carbon nanotube thin film transistor circuits and its application in organic light emitting diode control. *Nano Lett.* **11**, 5301-5308 (2011).

3. Goh, J. C., Chung, H. J., & Han, C. H. A new pixel circuit for active matrix organic light emitting diodes. *IEEE Electron Device Lett.*, **23**, 544-546 (2002).

4. Shirasaki, T, *et al*. Full-color polymer AM-OLED using ink-jet and a-Si TFT technologies. *SID Tech. Dig.* 1516-1517 (2004).

5. Lilien, O. M. History of industrial gravure printing up to 1920. 45–54 (Lund Humphries Publishers Ltd, London, 1972).

6. Jung, M. *et al.* All-printed and roll-to-roll printable 13.56-MHz-operated 1-bit RF tag on plastic foils. *IEEE Trans. Electron Device.* **57**, 571-580 (2010).

7. Lau, P. *et al*. Fully printed, high performance carbon nanotube thin-film transistors on flexible substrates. *Nano Lett*. **13**, 3864-3869 (2013).

8. Kawase, T. *et al*. Inkjet printing of polymer thin film transistors. *Thin Solid Films* **438-439**, 279-287 (2003).

9. Yan, H. *et al*. A high-mobility electron-transporting polymer for printed transistors. *Nature* **457,** 679-865 (2009).

10. Shin, K. *et al*. Roll-to-roll gravure printing of thick-film silver electrode micropatterns for flexible printed circuit board. *J. Coat. Technol. Res*., **14** (1) 95-106 (2017).

11. Leppamiemi, J. *et al*. Rapid low-temperature processing of metal-oxide thin film transistors with combined far ultraviolet and thermal annealing. *Appl. Phys.Lett*. **105**. 113514 (2014).

12. Nakano, M. *et al*. Control of major carriers in an ambipolar polymer semiconductor by self-assembled monolayers. *Adv, Mater*. **29**.1602893 (2017).

13. Haratipour, N. *et al*. Fundamental limits on the subthreshold slope in schottky source/drain black phosphorus field-effect transistors. *ACS Nano* **10**. 3791-3800 (2016).

14. Kim, T. *et al*. Electrical properties of synthesized large-area MoS_2 field-effect transistors fabricated with inkjet-printed contacts. *ACS Nano*. **10**. 2819-2826 (2016).

15. Koo, H. *et al.* Scalability of carbon-nanotube based thin film transistors for flexible electronic devices manufactured using an all roll-to-roll gravure printing system. *Sci. Rep.* **5**, 14459; doi:10.1038/srep14459 (2015).

16. Lee, J. *et al*. Register control algorithm for high resolution multilayer printing in the roll-to-roll process. *MSSP*. **60-61**,706-714 (2015).

17. Noh, J. *et al.* Key issues with printed flexible thin film transistors and their application in disposable RF sensors. *Proc. IEEE.* **103**, 554–566 (2015).

18. Lee, W. *et al.* A fully roll-to-roll gravure-printed carbon nanotube-based active matrix for multi-touch sensors. *Sci. Rep.* **5**, 17707; doi: 10.1038/srep17707 (2015).

19. Sun. J. *et al.* Proving scalability of an organic semiconductor to print a TFT active *matrix* using a roll-to-roll gravure. *ACS Omega* **2**, 5766-5774 (2017).

20. Cao, X. *et al*. Fully screen-printed, large-area, and flexible active-matrix electrochromic displays using carbon nanotube thin-film transistors. *ACS Nano* **10**, 9816-9822 (2016).

21. Gelinck, G., Heremans, P., Nomoto, K., & Anthopoulos, T. D. Organic transistors in optical displays and microelectronic applications. *Adv. Mat.* **22**, 3778-3798 (2010).

22. Kopola, P. *et al*. Gravure printed organic light emitting diodes for lighting applications. *Thin Solid Films* **517**. 5757-5762 (2009).

23. Stranks, S. D., Baker, A. M. R., Alexander-Webber, J. A., Dirks, B. &, Nicholas, R. J. Production of high-purity single-chirality carbon nanotube hybrids by selective polymer exchange. *Small* **9**, 2245−2249, (2013).

24. Stranks, S. D., Habisreutinger, S. N., Dirks. B., & Nicholas, R. J. Novel carbon nanotube-conjugated polymer nanohybrids produced by multiple polymer processing. *Adv. Mater.* **25**, 4365–4371, (2013).

25. Ding, J. *et al.* Enrichment of large-diameter semiconducting SWCNTs by polyfluorene extraction for high network density thin film transistors. *Nanoscale* **6**, 2328−2339, (2014).

26. Ding, J. *et al.* A hybrid enrichment process combining conjugated polymer extraction and silica gel adsorption for high purity semiconducting single-walled carbon nanotubes (SWCNT). *Nanoscale* **7**, 15741−15747, (2015).

27. Li, Z. *et al.* Raman microscopy mapping for the purity assessment of chirality enriched carbon nanotube networks in thin-film transistors. *Nano Research.* **8**, 2179−2187. (2015).

28. Sirringhaus, H. *et al*. High-Resolution Inkjet Printing of All-polymer Transistor Circuits. *Science* **290**. 2123-2126 (2000).

29. Kim, D. *et al*. Fully Gravure Printed Complementary Carbon Nanotube TFTs for Clock Signal Generator Using Epoxy-Imine Based Cross-linker as n-Dopant and Encapsulant. *Nanoscale* **47**.19876-19881 (2016).

30. Yang, Y. *et al*. Low Hysteresis Carbon Nanotube Transistors Constructed via a General Dry-Laminating Encapsulation Method on Diverse Surfaces. *ACS Appl. Mater. Interfaces.* **9**.14292-14300 (2017).

31. Ha, T. *et al*. Highly Stable Hysteresis-Free Carbon Nanotube Thin-Film Transistors by Fluorocarbon Polymer Encapsulation. *ACS Appl. Mater. Interfaces*. **6**. 8441-8446 (2014).

32. Homenick, C. *et al*. Fully Printed and Encapsulated SWCNT-Based Thin Film Transistors via a Combination of R2R Gravure and Inkjet Printing. *ACS Appl. Mater. Interfaces*. **8**. 27900-27910 (2016).

33. Yeom, C. *et al*. Large-area compliant tactile sensors using printed carbon nanotube active-matrix backplanes. *Adv. Mat.* **27**. 1561-1566 (2015).

34. Lefebvre, J, J. *et al*. High-purity semiconducting single-walled carbon nanotubes: a key enabling material in emerging electronics. *Acc. Chem. Res*., **50**. 2479-2486 (2017).

Figure legends

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

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

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

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