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## Letter

# Polypyrrole top-contact electrodes patterned by inkjet printing assisted vapor deposition polymerization in flexible organic thin-film transistors

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## ABSTRACT

Highly conductive polymer, polypyrrole (PPy) was successfully patterned as source and drain (S/D) electrodes for flexible pentacene thin film transistors in top-contact structure by combining inkjet printing and vapor deposition polymerization. Facile inkjet printing of initiator and subsequent exposure of pyrrole monomers resulted in selective absorption and polymerization of pyrrole monomers on the patterned initiator region. Pentacene transistors based on printed PPy electrodes exhibited higher electrical characteristics than that of the devices with thermally evaporated Au electrodes. Improved performance of the devices based on PPy electrodes could be attributed to the reduction of contact resistance at the interface between polymer and organic semiconductor. For the replacement of metal electrodes, vapor deposition polymerization assisted inkjet printing technique can provide a versatile method to utilize highly conductive polymer as a functional electrode of flexible organic electronic devices.

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## 1. Introduction

The development of a printing process for the fabrication of organic thin-film transistors (OTFTs) has focused on printed flexible electronics. Among established printing methods, including inkjet printing (IJP) [1], spray printing [2], screen printing [3], and  $\mu$ -contact printing [4], IJP has received attention because it is a direct, simple process that can print over a large area, does not leave residual ink due to drop-on-demand patterning, and is widely compatible with various materials without the need for a pre-patterned mold or mask. Recently, a customized high-resolution inkjet printer designed specifically for laboratory and industrial use was developed and distributed. However,

conventional desktop inkjet printer enables low-cost fabrication of printed patterns using word-processing software.

Conducting polymers are promising materials as printable electrodes for flexible electronic devices due to their high conductivity and environmental stability [5]. However, most conductive polymers cannot be dispersed in common solvents; thus, little attention has been paid to these conducting materials and their application as S/D electrodes for printed electronics. Few studies have reported the use of patterned conducting polymers in OTFTs for printing S/D electrodes using different methods and structures. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) via IJP acted as functional S/D electrodes with a bottom-gate, bottom-contact structure [6]. Wang et al. studied inkjet-printed S/D PEDOT:PSS with top-gate geometry in polymer TFTs [7]. Patterning electrodes based on polyaniline-poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) (PANI-PAAMPSA) were printed

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on a silane-treated substrate by  $\mu$ -contact printing in bottom-contact transistors [8]. Stamping technique with PEDOT S/D electrodes for bottom-contact OTFTs was reported by Li et al. [9]. These reports, all of which used water-dispersive conducting polymers as electrodes for printed patterns, showed relatively low device performance compared with Au S/D electrode devices or good performance with different printing methods. The integration of nondispersive conducting polymer materials into top-contact OTFTs by inkjet printing technique has been a challenge in flexible electronics.

Vapor deposition polymerization (VDP) has been suggested as a method for thin-film electrode of conducting polymers. In VDP, vaporized monomers absorb only on an initiator and subsequently facilitate the polymerization of pyrrole. VDP, introduced in our previous report [10], was used to modify inorganic nanomaterials with polymer, resulting in a new type of nanomaterial with an inorganic-polymer core-shell structure.

Here, we introduce a versatile route to overcome the limitations of printing nondispersive conducting polymer PPy by combining inkjet printing with vapor deposition polymerization (IJP-VDP) for the fabrication of top-contact S/D electrodes in flexible OTFTs. PPy was chosen because it could be substituted for expensive Au electrodes and opened a way to pattern of nondispersive conducting polymer in common solvents. An initiator solution was deposited on the organic semiconductor layer by IJP, and subsequent exposure to vaporized monomers induced selective polymerization, producing a conducting polymer on the printed initiator. IJP-VDP is emerging as a useful method for printing an electrode pattern of nondispersive conducting polymers in top-contact OTFTs instead of metal electrodes. To the best of our knowledge, this is the first report of high-performance flexible pentacene transistors with top-contact S/D electrodes of a patterned conducting polymer using IJP-VDP, where illustrate the simplicity and versatility of the patterning process with a nondispersive conducting polymer.

## 2. Experimental

Pyrrole, ammonium persulfate (APS, 98%), and poly(4-styrenesulfonate) (PSS, 30 wt.% in H<sub>2</sub>O, Mw ~70,000 g/mol) were purchased from Sigma–Aldrich Co. Ltd. and used as a monomer, an oxidant, and an additive, respectively. Pentacene (99.995% trace metals basis) as an organic semiconductor, poly(4-vinylphenol) (PVP, Mw ~20,000 g/mol) as a dielectric, Poly(melamine-co-formaldehyde) as a cross-linking agent, and propylene glycol methyl ether acetate (PGMEA) as a solvent were also bought from Sigma–Aldrich Co. Ltd. Polyethylenesulfone (PES) film was supported by i-component Co. Ltd. and used as a flexible substrate. All chemicals were used as received.

The device was built on a flexible PES film. The Au gate electrode (50 nm) was thermally deposited on the PES substrate at a deposition rate of  $1.0 \text{ \AA s}^{-1}$ . PVP, a polymeric dielectric material, and poly(melamine-co-formaldehyde), a cross-linking agent, were dissolved in PGMEA (10 mL) at a molar ratio of 2:1. The PVP solution was spin-casted

at 4000 rpm for 30 s and subsequently cross-linked at  $130 \text{ }^\circ\text{C}$  for 15 min and  $200 \text{ }^\circ\text{C}$  for 5 min in N<sub>2</sub> atmosphere, forming a ~300-nm PVP gate dielectric. On top of the cross-linked PVP dielectric layer, pentacene film was thermally evaporated in a vacuum chamber by a shadow mask under a pressure of  $5 \times 10^{-6}$  Torr at room temperature at a deposition rate of  $0.4 \text{ \AA s}^{-1}$ . The pentacene semiconductor was ~60 nm thick. Prior to IJP-VDP, the pentacene layer was treated with O<sub>2</sub> plasma (80 W for 1 s) at ambient pressure. The initiator solution, composed of APS (20 wt.%) and PSS as an additive in distilled water (10 mL), was dropped on top of the pentacene active layer from the desktop printer cartridge (Cannon PIXMA IP 1300), in which the PSS concentration was varied from 0 to 12 wt.%. Devices with printed initiator patterns were exposed to pyrrole monomer vapor in a vacuum chamber at  $10^{-1}$  Torr for 10 min for VDP. For comparison, devices based on Au S/D electrodes were also fabricated with an identical corresponding structure.

Optical micrographs were acquired using a Leica DM2500 P. Infrared spectra were recorded using a Bomem MB 100 FTIR spectrometer. The plasma reactor was a parallel-electrode type with a 13.56-MHz radio-frequency generator. The conductivity of the printed PPy electrode was confirmed using four-probe measurements (Keithley 2400 source meter) at  $25 \text{ }^\circ\text{C}$ . The sheet resistance was averaged for 10 different locations in a PPy electrode. Transistor performance was characterized using an Agilent HP4155C semiconductor parameter analyzer. Capacitance voltage characteristics of the metal–insulator–metal (MIM) capacitors were measured using an HP 4284 precision LCR meter. Thicknesses of the thin films were measured using a profilometer (ET 3000, Kosaka Laboratory, Ltd.).

## 3. Results and discussion

Fig. 1 shows IJP-VDP patterning applied to the fabrication of S/D electrodes in an OTFT, exhibiting a well-defined PPy pattern with a channel length of ~135  $\mu\text{m}$  and thickness of ~450 nm. To confirm the polymerization of pyrrole monomers, Fourier transform infrared-attenuated total

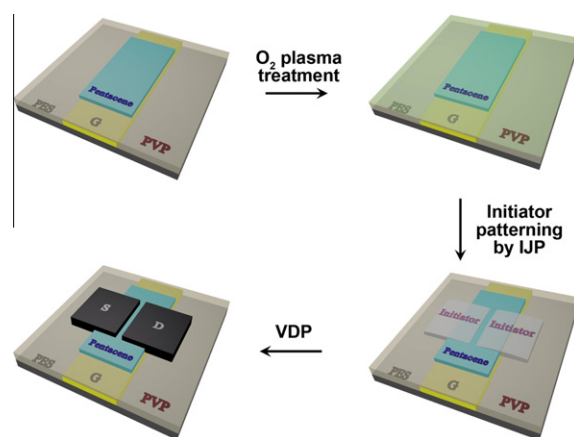


Fig. 1. Schematic illustration of PPy top-contact OTFTs fabricated via IJP-VDP.

reflection (FTIR-ATR) analysis was used. Peaks at 1549, 1410, and 723  $\text{cm}^{-1}$  were attributed to ring stretching, conjugated C–N stretching, and C–H wagging vibrations, respectively, and were in good agreement with FTIR spectra of PPy in our previous work [11]. The OTFT device with a bottom-gate, top-contact structure was built on a polyethylsulfone (PES) plastic film. We also fabricated a control device using evaporated Au as the top-contact S/D electrodes instead of printed PPy.

In IJP, the patterning resolution, or minimum feature accuracy, is affected by several factors, including properties of the substrate, ink viscosity, and printing method [12]. A stabilizer or surfactant, formulated with the proper viscosity and surface energy, is added to the conductive dispersive solution to modify ink properties for IJP applications [13]. We applied this modification to the initiator solution for IJP patterning of a nondispersive conducting polymer by using additives.

The edge waviness of printed PPy electrodes is shown in Fig. 2a. This phenomenon is often observed for IJP of conducting polymer patterns, inducing a large current variation compared with conventional evaporated metal electrodes with a shadow mask [14]. Thus, control of edge waviness is an important issue in the design of printed OTFTs. In this study, we obtained distinctive channel lengths according to the amount of PSS added to the initiator solution by IJP. The variation in PSS concentration (0–12 wt.%) correlated to the edge resolution and the surface resistance of the PPy electrode pattern, as shown in Fig. 2b. The protrusion edge decreased until PSS reached 6 wt.% and then increased from 6 to 12 wt.% PSS. After 6 wt.% PSS, clogging in the printer nozzle started, resulting in the collapse of the edge resolution in the printed pattern. Since PSS chains typically consist of a few hundred monomer units, even rather small differences in surface energy between the components in the initiator solution are sufficient to lead to almost complete surface pattern coverage by the lowest energy component of long chain length in PSS polymer, leading to reduce the edge protrusion of the pattern. Moreover, the surface resistance increased as the amount of polymeric PSS in the initiator solution increased.

The surface resistance of the PPy electrode pattern without PSS was measured at  $\sim 2.75 \times 10^3 \Omega/\text{sq}$  by the four-probe method and increased to  $\sim 8.61 \times 10^4 \Omega/\text{sq}$  with 12 wt.% PSS in ammonium persulfate (APS) solution. Arribas et al. demonstrated the synthesis of conductive PPy prepared by ferric chloride as oxidant with counterion PSS [22]. According to their results, the conductivity of PPy had little influence depending on the monomer/PSS ratio, while the enhancement of that was mainly attributed to the monomer/oxidant concentration. This provides strong evidence that the PSS do not play a role in conductivity enhancement. In this work, the sheet resistance is rather stable against changes until 9 wt.% of PSS concentration. The insulating property of PSS was found to result in an abrupt increase in sheet resistance at 12 wt.% PSS due to the hindrance of charge transport among polymer chains. With respect to both the edge resolution and the sheet resistance, the surface resistance was optimized at  $1.74 \times 10^4 \Omega/\text{sq}$  and 6 wt.% PSS, which was sufficient for application in organic electronic devices as an organic electrode [9,15,16]. Thus, conductive PPy patterns were achieved by modifying the initiator properties and using the proposed patterning process. Additionally, the vaporized pyrrole monomer was homogeneously deposited and polymerized directly on the printed oxidant pattern. The highly conductive polymer patterns were attributed to the continuous growth of a polymer film with no disconnections or cracks.

In order to check the electrical potential of the top-contact PPy electrodes fabricated by the proposed IJP-VDP method, thermally evaporated Au S/D electrodes were used in pentacene TFTs for comparison. Fig. 3 shows typical electrical output and transfer characteristics of a pentacene TFT with S/D electrodes of (a) PPy (PPy-OTFT) and (b) Au (Au-OTFT). Under our experimental conditions, a field-effect mobility of  $0.18 \pm 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a threshold voltage of  $-1.99 \text{ V}$ , and an on/off current ratio of  $3.23 \times 10^4$  were obtained in the PPy-OTFT (Fig. 3a). These results are comparable to the characteristics of the Au-OTFT with a field-effect mobility of  $0.15 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a threshold voltage of  $-10.09 \text{ V}$ , and an on/off current ratio of  $8.05 \times 10^4$  (Fig. 3b). In particular, the higher mobility of the PPy-OTFT

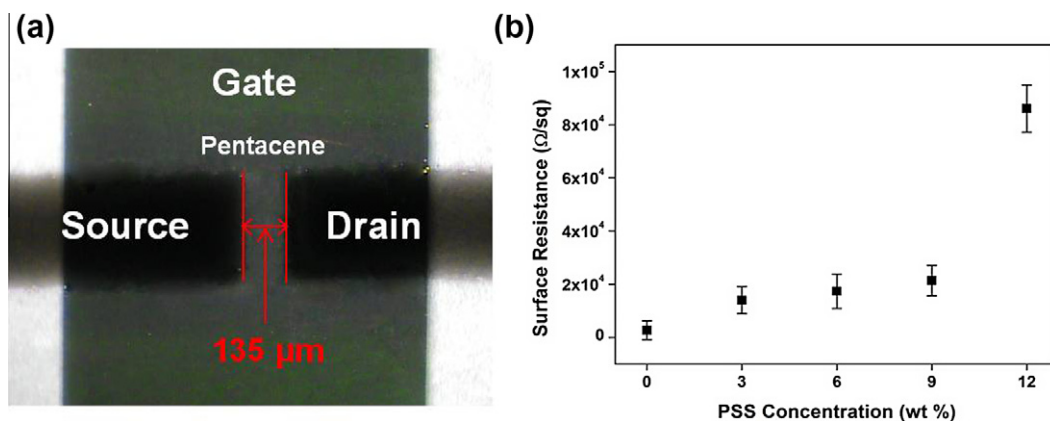


Fig. 2. (a) Optical image of patterned source and drain electrodes with PPy. (b) Surface resistances of PPy electrodes with different PSS concentrations.

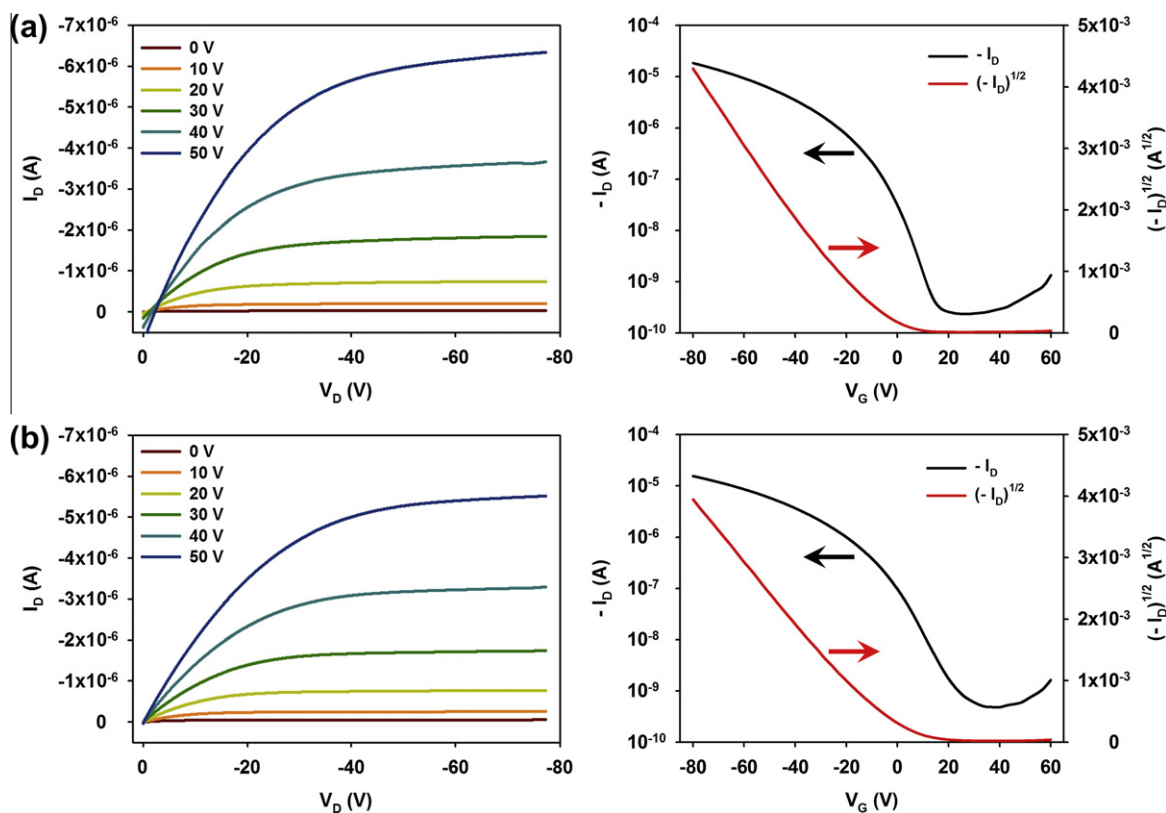


Fig. 3. Electrical output and transfer characteristics of the pentacene TFTs with source and drain electrodes of (a) PPY and (b) Au.

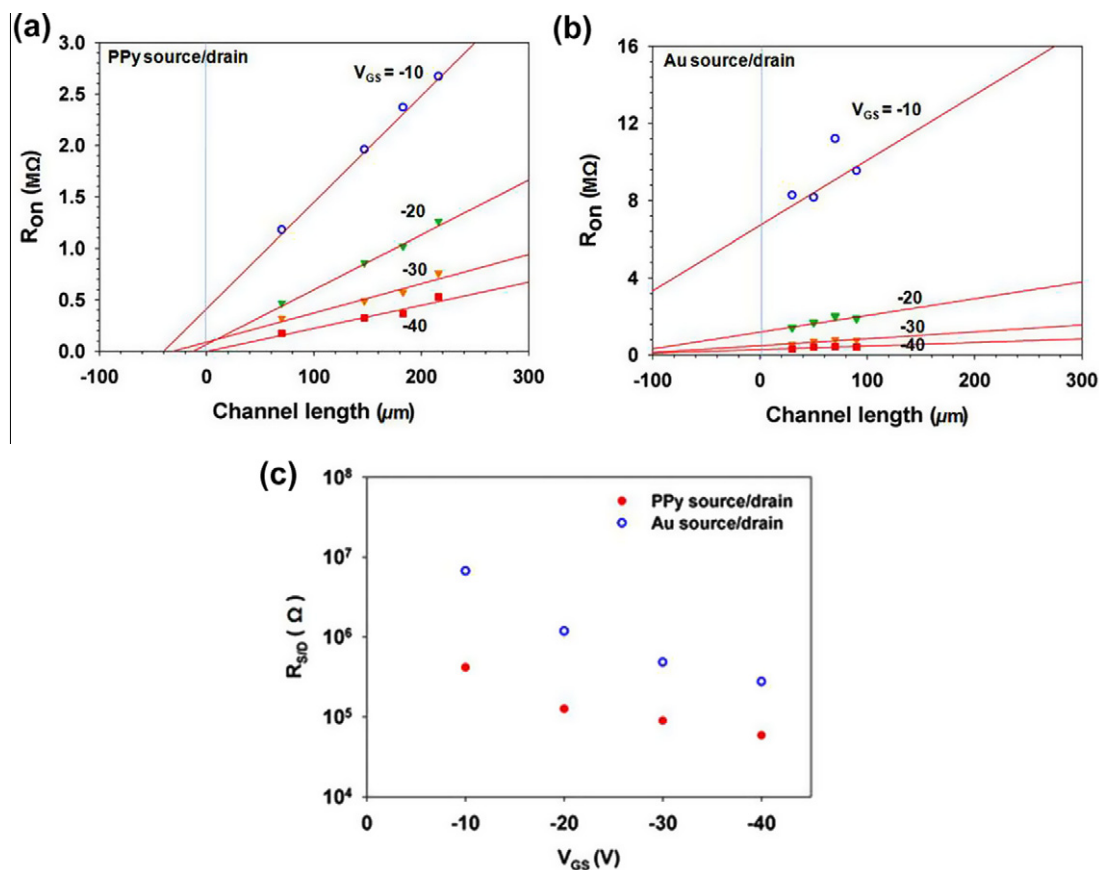
was obtained at the same voltage applied to the Au-TFT. The leakage current was less than a few nanoamperes in both cases, which is typical for OTFTs.

It is known that the  $R_c$  between the electrode and the organic channel is primarily caused by the charge-injection barrier formed at the interface that strongly dominates the charge injection properties. Hill et al. [18] previously reported that the electronic structure of most metal–organic molecular semiconductor interface has the simple Schottky–Mott limit and exhibits a substantial interfacial dipole barrier, where a significant fraction of the interface dipole barriers at the interfaces corresponds to a lower metal work function due to adjacent organic molecules. In the case of a polymer–polymer interface, a conducting polymer has fewer free electrons than a metal. Its work function does not have a significant surface electron tail contribution and does not change, unlike the modification on a metal–polymer surface. This, in turn, makes it possible to form smaller hole-injection barriers at the interface between the polymer electrode and organic semiconductor compared with the Au electrode/pentacene contact even though both metal and polymer electrodes have similar work function [19].

We investigated the  $R_c$  of PPY and Au electrodes using the transfer-line method (TLM) (ESI†). When the on-resistances ( $R_{on}$ ) for low  $V_{DS} = -2$  V were normalized, linear ohmic contacts were observed with increasing channel length. As shown in Fig. 4, the  $R_c$  decreased with  $V_G$  becoming more negative for both Au-OTFTs and PPY-OTFTs. Such

a decrease in  $R_c$  with more negative  $V_G$  is correlated to the higher density of charge in the conducting channel in the large channel-length regime [17]. For the Au-TFT patterns from TLM, the corresponding channel resistance was measured at a gate voltage of  $-30$  V, providing a slope ( $R_s/W$ ) of  $4.1 \times 10^5 \Omega/\text{sq}$ , similar to that of the PPY-TFT shapes from TLM. Especially, the  $R_c$  of the printed PPY electrodes was approximately one order of magnitude lower than that of the Au electrodes. These results suggest that the channel resistance of both TFTs was similar regardless of contact; thus, reduced contact resistance was a primary reason for the increased mobility.

The slight decrease in the on/off current ratio and slight increase in the subthreshold slope of the printed PPY-TFTs are thought to be related to the formation of pentacenequinone during surface treatment of pentacene by IJP (Fig. 3). In the fabrication process,  $O_2$  plasma treatment was used to increase the surface energy of the pentacene semiconductor surface layer for printing the initiator solution to form a uniform PPY electrode. However,  $O_2$  plasma plays an important role in obtaining successful initiator patterns on the pentacene surface and also limiting device performance. The conjugated carbons of pentacene were functionalized to C–O or C=O groups by  $O_2$  plasma treatment [20], resulting in the formation of charge-scattering sites in the molecules. To minimize pentacene damage for carrier transport and maximize device performance,  $O_2$  plasma treatment was conducted at 80 W for 1 s. Subsequently, PPY S/D electrodes were baked for 10 min at



**Fig. 4.** Channel width-normalized contact resistance in devices with source/drain electrodes of (a) PPy and (b) Au. (c) Total contact resistance ( $R_{SD}$ ) of both PPy and Au OTFTs as a function of applied gate voltage.

100 °C after IJP-VDP to remove residual moisture and increase electrical performance [21].

#### 4. Conclusion

OTFTs with conducting polymer S/D electrodes were fabricated by the proposed IJP-VDP method. In particular, the substitution of expensive Au electrodes to nondispersive conducting polymer PPy with top-contact structure was demonstrated for the first time in this work. Pentacene transistors based on printed PPy electrodes exhibited electrical characteristics superior to those of transistors based on thermally evaporated Au electrodes. Patterned PPy electrodes had low contact resistance at the semiconductor interface, resulting in the improved performance. This approach offers a practical strategy for patterning a nondispersive conductive polymer electrode by combining direct-write printing with VDP for flexible electronic devices.

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