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Recent progress on electrohydrodynamic nanowire printing

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ABSTRACT Electrohydrodynamic nanowire printing (e-NWP) technology can be used to print ultra-fine nanowires (NWs) in patterns at high precision. This technology has enabled advances in large-area patterned NWs, high-precision and high-integration devices, nanoelectromechanical systems, and bio-inspired devices. The electrical properties of the devices printed using e-NWP can be adjusted by controlling the gaps and diameters of the NWs. These forms have widespread application in field effect transistors, synaptic mimicry and masks. This review summarizes the basic principles, materials, printing methods and applications of e-NWP, and then outlines the research direction and obstacles that should be overcome to expand the applications of e-NWPs, and enable their commercialization.

Keywords: electrohydrodynamic nanowire printing, nanowire array, polymer, oxide nanowires, lithography

INTRODUCTION

This review focuses on the evolution and application of the electrohydrodynamic nanowire printing (e-NWP) [1–3]. e-NWP can be used to precisely control the deposition of nanofibers (NFs) for use in printing of flexible electronics, micro-nanosize devices, and biological tissues [1,4–22]. Therefore, the deposition of NFs in orderly arrangements has achieved wide applicability in electrostatic spinning technology [23–74].

The main methods to prepare ordered electrospun NFs include the roller method, the parallel-electrode method, the patterned-electrode method [32] and the near-field electrospinning (nf-ES) method [75–116]. Early development of electrospinning equipments focused mainly on the nozzle and receiver [75,77–81]. To reduce the danger

and high energy consumption that are caused by the high voltage of electrostatic spinning, researchers developed low-voltage electrospinning by increasing the auxiliary effect of external forces to reduce the electric field force [75]. Subsequently, the components of spinning liquid components, and the adjuvants were modified to have special properties [76]. Then nf-ES was developed to reduce the spinning distance and therefore the required intensity of electric field [78]. In 2003, a triangular thin film tip was adapted as a spinning tip; this method reduced the spinning distance to 2 cm, and spinning voltage to 3–4 kV. This method allows nf-ES at low voltage, and obtains orderly arrangement of microfibers or NFs by rotating a collection plate relative to the tip [75]. nf-ES has been applied to electronic devices, photovoltaics and biology [76–144] (such as human gesture recognition [113], and controlling of cell orientation [114]).

e-NWP was introduced in 2013 [1]; it overcame the demerits of traditional electrospun fibers such as disorder and poor control in position, and realized precise manipulation of single nanowires (NWs). e-NWP allows preparation of highly-ordered polymer NWs, metal doped organic NWs (ONWs) and metal-film NWs on flexible substrates with high efficiency on a large area [8–10,13,17,20]. By use of e-NWP, the diameter, number and position of NWs can be controlled according to the requirement of the NW array, thus avoiding the need for secondary operations to align the NWs [1,4–22].

Electronic devices based on NWs show high integration, low energy consumption and flexibility [4–6,8–10,12–18,20]. e-NWP can be used to adjust the electrical properties of the device for applications in field effect transistors (FETs), sensors, memories, and bio-mimetic

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devices. The electrical properties of the device can be adjusted by controlling the number of printed NWs, and the gap between them. e-NWP has potential applications to fabricate flexible wearable sensors, electronic textiles, transistors and precision integrated circuits.

MECHANISM

e-NWP technology can realize accurate and controllable printing of NWs or NFs. The basic principle of e-NWP is to convert the printing ink into a straight solidified NW under high electrical field before printing it onto the substrate. The NWs are cylindrical instead of flaky. It is also the difference between e-NWP and electrohydrodynamic jet printing. This goal is achieved by controlling the tip-to-collector distance ($d_{(t,c)}$) to < 1 cm, and reducing the voltage of e-NWP [1] (Fig. 1). The NW solidifies before it is printed onto the substrate (Table 1). During e-NWP, the ink flows in a jet from the probe tip, and the printing voltage (V_p) is about 0.5–3.6 kV. A collection plate is placed on a two-dimensional (2D) moving platform, and it is moved under control to realize fixed-point printing of patterns in a plane.

DIFFERENT TYPES NWs AS OBTAINED FROM e-NWP

Polymers are the best choice for electrospinning materials because of their one-dimensional (1D) linear structure and useful range of properties, such as viscosity, flexibility and strength. Polymer materials that are used in e-NWP include poly(ethylene oxide) (PEO) [1,17,18], poly(4-vinylphenol) (P4VP) [17,22], polyvinyl carbazole (PVK) [16,19], poly(3-hexylthiophene) (P3HT) [10,15] and poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE)

[9]. According to the requirements of electrospinning, polymers can be used in pure form or in blends.

Pure polymer NWs

PVK NWs were aligned with PVK styrene solution using e-NWP (Fig. 2) [1]. Fig. 2a shows that PVK NWs not only possess nanoscale dimensions (290 nm), but also can realize a large-scale high-regularity array; Fig. 2b shows that the PVK NWs have a regular circular cross section. The e-NWP PVK NW can be removed after depositing metal films as a shadow mask to make a channel (Fig. 2 c). In addition, the different diameters of PVK NWs can be attained by adjusting the PVK concentration (2.93, 3.96, 4.72, 5.71 or 6.19 wt%) which follows the scaling relationship ($D \sim \rho^{1.68}$). The diameter of PVK NW is 290 nm. The scaling relationship in e-NWP is consistent with the relationship of the conventional electrospinning method ($D \propto \rho^{\delta}$). Other polymers can be printed by e-NWP using a suitable solution, such as (1) aligned PVK NWs using PVK styrene solution (Fig. 2) [1]; (2) PVDF-TrFE (75:25, Solvay) (15 wt%) dissolved in a solvent mixture of *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) ($w:w = 1:4$, $V_p = 1.1$ kV, $d_{(t,c)} = 7$ mm) [9]; (3) 30 wt% P4VP in dimethylformamide/ethanol solution ($w:w = 60:0$, $V_p = 1.4$ kV, $d_{(t,c)} = 7$ mm) [8]; and (4) P3HT/toluene solutions (0.2, 2, and 5 wt%, $V_p = 1.8$ kV, $d_{(t,c)} = 1$ mm) [22].

Blended polymer NWs

Compared with pure polymers, blended polymers have the electrostatic interaction between two blended components. This can make impossible-to-print polymers be printed into NWs by adjusting viscosity and surface

Figure 1 Diagram of electrohydrodynamic nanowire printing setup. Reprinted with permission from Ref. [1]. Copyright 2013, Springer Nature.

Table 1 Parameters of printing methods, and quality of results

Method	$d_{(t,c)}$ (cm)	V_p (kV)	Homogeneity	Accuracy
ES	≥ 10	≥ 10	Bad	Bad
nf-ES	≤ 2	3–4	Excellent	Good
e-NWP	≤ 1	0.5–3.6	Excellent	Excellent

Figure 2 (a) Optical micrograph of well-aligned PVK NWs. (200 nm, scale bar); (b) field emission scanning electron microscopy (FESEM) image showing cross section of well-aligned PVK NW, which forms a perfect circle; (c) schematic illustration of the process for ONW lithography. Reprinted with permission from Ref. [1]. Copyright 2013, Springer Nature.

tension. The electronic properties of blended-polymer NWs can also have more versatility to be adjusted according to needs. Large-area poly{[N,N-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5-(2,2-bithiophene)} (N2200):PEO-blend NW ($w:w = 7:3$) arrays were printed using a high-speed e-NWP, from a blend of N2200 and PEO in trichloroethylene and chlorobenzene cosolvents [1]. e-NWP has been used to print organic polymers in various configurations. Core-sheath-structured P3HT/PEO NWs have been prepared using blends of P3HT/PEO 70:30 (w/w) [18]. Highly-aligned P3HT NWs doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) have been achieved ($V_p = 1.5\text{--}2$ kV, $d_{(t,c)} = 7$ mm) [15]. Patterned nano-scaled structures of polyvinylpyrrolidone (PVP), PEO and tetracycline hydrochloride composites have been printed [11]. PEDOT:PSS-PEO composites were printed by adding 1 $w/v\%$ PEO directly to conductive PEDOT:PSS solution (1.0 wt% in water) to create PEDOT:PSS-PEO solution [7]. Furthermore, thiophene diketopyrrolopyrrole (FT4-DPP):PEO NWs have been achieved by printing FT4-DPP:PEO (7:3, $w:w$)/chloroform solution (Fig. 3) [5]. These methods achieved the printed NWs of blending polymer, and broadened the

Figure 3 Fabrication of aligned (FT4-DPP):PEO NWs. (a) Schematic illustration of electrospinning of aligned (FT4-DPP):PEO NWs between parallel electrodes. (b) Polymer chain alignment during polymer solution jetting by high-electric-field and strong shear force. (c) Schematic illustration of transfer process of single aligned (FT4-DPP):PEO NW onto the substrate. (d) Histogram of diameter distribution of (FT4-DPP):PEO NW. Optical images of FETs on SiO_2/Si substrate and Au S/D electrode with (e) single and (f) multiple (FT4-DPP):PEO NWs. Reprinted with permission from Ref. [5]. Copyright 2018, John Wiley and Sons.

range of e-NWP materials.

Metallic NWs

Cu NFs can be produced by adding PVP and Cu(II) trifluoroacetate to a mixture of DMF and THF solvents [20]. Printing of PVP/(Cu(CO₂CF₃)₂) composite NF array by e-NWP on the substrate (Fig. 4), followed by calcination in air at 500°C for 1 h, then calcination in H₂ at 300°C for 1 h yielded the Cu NF array. The average diameter of Cu NF was 710 ± 90 nm. The energy-dispersive X-ray spectroscopy (EDS) spectrum (Fig. 4b–d) showed that polymer and precursor were decomposed after the calcination at 500°C in air, and the CuO NFs were reduced to Cu NFs at 500°C in H₂. Aligned composite NFs with constant spacing of 100 μm were shown in Fig. 4d. Parallel and

Figure 4 (a) Process to print CuO NF and Cu NF array with polymer and ink composed of a solution of metal precursors. SEM images and EDS spectra of (b) a PVP/Cu(CO₂CF₃)₂ composite NF, (c) a CuO NF, and (d) a Cu NF (1 μm, scale bar). SEM images of parallel and perpendicular patterns of (e) PVP/Cu(CO₂CF₃)₂ composite NF and (f) Cu NF (100 μm, scale bar). (g) Current-voltage (*I*-*V*) curve of single Cu NF aligned between two gold electrodes with a gap of 100 μm (an SEM image of the electrodes/nanofiber is shown in the inset; scale bar: 50 μm). (h) UV-vis spectrum of parallel patterns of Cu NF array on the glass substrate. Reprinted with permission from Ref. [20]. Copyright 2014, John Wiley and Sons.

perpendicular patterns of Cu NF arrays were achieved (Fig. 4f). It shows that resistivity of e-NWP Cu NF (14.1 μΩ cm) is lower than that of the previously reported electrospun Cu NF (120 μΩ cm) (Fig. 4g). The parallel patterns of Cu NF array on the glass show more than 98% transmittance in the visible range (Fig. 4h). This method achieved the printed transparent NWs of Cu oxide or Cu, and broadened the range of e-NWP materials.

e-NWP can also produce long Type III Ag NWs (Fig. 5) [10] without breaks by using a strong electric field to jet a highly viscous PVP and metal precursors from the syringe. Low resistivity ($\rho = 5.7 \mu\Omega \text{ cm}$), low sheet resistance ($R_s \approx 26.9 \Omega \text{ sq}^{-1}$) and high transmittance ($T > 92\%$, in visible range) of e-NWP Ag NWs with an average diameter of 695 nm were shown in Fig. 5d–g. The polymer and metal precursors solidify into composite NWs by evaporation. The composite NWs become Ag NWs after calcination from PVP with the CuO frame structure. It is

an improved method which avoids the use of H₂ gas in the reduction process.

Al-NF electrodes can be produced by lithography around PVK NFs mask [13] (Fig. 6). The interfiber separation (70 μm) and the average diameter ($1.11 \pm 0.12 \mu\text{m}$) of PVK NF was shown in Fig. 6b, c. The fibers can separate the Al layer very effectively by depositing 40 nm Al on the PVK NFs arrays (Fig. 6d). The fiber pixel separators can be detached by the taping method (Fig. 6f, g). This work suggests that e-NWP can be used to fabricate highly aligned organic NF arrays to pattern organic light-emitting diodes (OLEDs).

Similarly, Au-plated NWs were prepared by depositing an Au layer on P4VP NWs [8] (Fig. 7). First, Au nanoparticles were produced by the vapor of hydrazine monohydrate. Then Au precursor was adsorbed to the P4VP NW surface by electrostatic interaction after (1) complexation, (2) reduction, and (3) coarsening at room

Figure 5 (a) Simulation diagram of the printing process of Type III-highly-aligned Ag NWs array with polymer and metal precursors mixed solution ink and SEM image of the composite NW; (b) SEM images of grid-patterned Ag NW arrays (100 μm, scale bar); (c) digital image of Ag NW array on flexible polyimide film. (d) Bending stability of AgNW/PI and indium tin oxide (ITO)/polyethylene terephthalate (PET) against bending cycles (inset: R/R_0 vs. bending radius of AgNW array and ITO). (e) I - V curve of Ag NW. (f) Optical transmittance and (g) haze characteristics of Ag NW arrays with different patterns and pitch size in the visible range. Reprinted with permission from Ref. [10]. Copyright 2016, John Wiley and Sons.

Figure 6 (a) Schematic illustration of Al NF pixel separators in OLEDs. (b) Optical micrograph of a PVK NF array with 70 μm interfiber separation. (c) SEM image of a PVK NF with diameter of 1.01 μm. (d) Cross-sectional SEM image of PVK NFs on which 40 nm thick Al was deposited. Inset is a schematic illustration of the SEM image. (e) SEM image of a PVK NF on which 170 nm thick LiF was deposited. (f) Schematic illustration showing the principle of e-NWP. (g) SEM image of separated LiF layer after removing the PVK NF. Reprinted with permission from Ref. [13]. Copyright 2016, John Wiley and Sons.

temperature. The total resistance followed the behavior of parallel resistors (Fig. 7b). The optical transmittance of parallel patterned Au NW arrays with different wire spacing showed that the Au array can be used as a transparent electrode (Fig. 7c). This work suggests that metallic NWs can be used as flexible nanoelectrodes (NEs) by e-NWP and metallization process on a flexible plastic substrate at room temperature. An Au NW electrode array can be produced at room temperature by using these aligned P4VP NW templates [8]. Pure metal precursors cannot be printed using e-NWP, but it is possible with selected polymer binders. The metal precursors can then be printed together with the polymer, which can be removed later through further calcination and reduction processes to remain pure metallic NWs.

APPLICATIONS OF e-NWP PRINTED NANOWIRES

Field-effect transistor

The effect of annealing on the regularity of F4-TCNQ/P3HT NW was shown in Fig. 8a, b [15]. After the in-

corporation of F4-TCNQ in P3HT, the two molecular chains aggregated due to the strong electrostatic interaction between the F4-TCNQ and the P3HT chain. The F4-TCNQ molecule has great rigidity, but at high temperature, the P3HT chain was oriented rapidly. The P3HT chains were confined in the core structure and the PEO sheath in the internal structure of NW before annealing was more regular along the axis, which enhanced the charge transfer. The FETs of undoped P3HT and F4-TCNQ/P3HT NW showed typical behavior of p-type organic FETs (Fig. 8c, d). With the increase of the ratio of F4-TCNQ, the maximum on-current and field effect mobility (μ_{FET}) of FET increased (Fig. 8e).

However, the properties of doped FET before thermal annealing was not excellent. The performance of P3HT NW FET doped with F4-TCNQ before annealing was even lower than that of undoped P3HT NW devices. On the contrary, the device performance of annealed doped P3HT NW FET was significantly improved. After thermal annealing at 200°C, the on-current and the μ_{FET} incidentally increased by tens of times ($\mu_{\text{FET}} = 9.78 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) compared with that before annealing.

Figure 7 (a) Schematic illustration of the process to prepare a well-aligned template NW array and the electroless Au plating procedure on P4VP NW. (b) Total resistance and resistivity of electroless plated Au NWs with different numbers of wires. (c) Optical transmittance of Au NW arrays with different wire spacing. Reprinted with permission from Ref. [8]. Copyright 2017, American Chemical Society.

Figure 8 Schematic illustration of the microstructure change of P3HT/FT4-DPP chain with thermal annealing: (a) before and (b) after annealing. Transfer characteristics (I_D - V_G) of F4-TCNQ/P3HT NW FET with various concentrations (c) before and (d) after thermal annealing at 200°C for 1 h. (e) μ_{FET} of F4-TCNQ/P3HT NW FETs before (black line) and after (red line) annealing. (f) μ_{FET} (black line) and maximum on-currents (red line) of F4-TCNQ/P3HT NW FETs with different annealing temperatures. Reprinted with permission from Ref. [15]. Copyright 2017, American Chemical Society.

These results were also consistent with the annealing temperature dependence of electrical properties in F4-TCNQ/P3HT NW FETs. With annealing temperature

increasing by 100, 150, 200°C in P3HT NW FET doped with 1wt% F4-TCNQ, the maximum on-current level and maximum μ_{FET} of doped NW FET increased (Fig. 8f).

FETs obtained using e-NWP printed with different materials showed reasonable properties of carrier mobility, contact resistivity and ON/OFF ratio (Table 2). P3HT-PEO NW FET showed the highest carrier mobility of $9.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and very low contact resistivity of $5.53 \text{ } \Omega \text{ cm}$, but ON/OFF ratio (1.38×10^5), whereas metal-based NW FETs had ON/OFF ratio on the order of 10 [8] (Table 2).

Complementary inverter was fabricated by aligning well-parallel P3HT/PEO NWs and N2200/PEO NWs array on the shape-specific Ti/Au electrodes with length of 50 nm on a Si/SiO₂ (100 nm) substrate (Fig. 9a, c and e) [1]. The continuous switching action of the P3HT/N2200 NW complementary inverters is also shown, which is directly related to the parasitic capacitance and resistance of the devices. The average transfer delay of the P3HT/N2200 NW inverters was almost 1 ms, and a counter-mirrored voltage characteristics of the inverters were obtained by the source measurement tool. In addition, the complementary inverter showed the typical switching characteristic with gain of ~ 17 (Fig. 9d). Compared with other methods, e-NWP can print long, continuous and digitally aligned NWs in one step, without secondary processing. Secondly, the diameter of NWs can be controlled by solution concentration and viscosity, which is an easier process than EBL, and other traditional lithographic techniques.

Ferroelectric memory

Non-volatile polymer memory has been achieved by using high-throughput direct e-NWP [18]. Polymer semiconducting P3HT:PEO (70:30, w/w) NWs channel

Table 2 Field-effect transistor properties of NWs printed with different materials by e-NWP

Material of NW	Carrier mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Contact resistivity ($\Omega \text{ cm}$)	ON/OFF ratio	Ref.
P3HT-PEO	9.7	5.53	1.38×10^5	[1]
FT4-DPP:PEO	7.46 ± 0.53	-	-	[5]
P4VP-Au	3.5 ± 1.0	24.8	-	[8]
PVDF-TrFE-Ag	0.67	-	-	[9]
P3HT-PEO:Cu,Ag	5.49 ± 1.47	7.9×10^4	5.93×10^8	[10]
P3HT-F4-TCNQ	0.00800	-	2.48×10^4	[15]
P3HT-F4-TCNQ (after annealing)	0.00978	-	1.28×10^5	[15]
P3HT	0.008	-	1.6×10^3	[22]
P3HT (ODTS surface)	0.045	-	2.1×10^4	[22]

Figure 9 (a) Large-area single P3HT:PEO-blend (70:30, w/w) NW FET array (7 cm × 7 cm) with ~300 nm channel length (144 bottom-contact devices). (b) Histogram of the mobility for large-area P3HT:PEO-blend NW FET array with an average of 3.8 ± 1.6 cm² V⁻¹ s⁻¹. (c) Large-area single P3HT:PEO-blend NW FET array on polyarylate (PAR) substrate. (d) Input-output voltage characteristic for complementary inverter circuit based on P3HT/PEO NWs and N2200/PEO NWs (inset: gain characteristics). (e) Optical image of inverter array (left, scale bar, 2 mm) and schematic illustration of an inverter (right) Ref. [1]. Reprinted with permission from [1]. Copyright 2013, Springer Nature.

and ferroelectric (PVDF-TrFE) insulator were aligned in the polymer memory. The distribution of both ON current values and ON/OFF ratios was calculated. The devices had distinct bistable ON and OFF current states for memory operation, and the depleted state of P3HT channel was retained after a positive gate voltage was removed. To control the memory properties, the number and location of wires can be adjusted (Fig. 10d, e). The device with 16 wires had ON/OFF ratio >100, which was sufficient for non-volatile memory operation. The memory showed characteristic current hysteresis > 10⁴ s

(Fig. 10f) and write-erase endurance for 120 cycles (Fig. 10g). The flexible polymer NW memory device tolerated > 1000 bending cycles to a bending radius of 5.8 mm. This work creates a highly flexible and non-volatile memory. The performance of memory can be controlled by adjusting the number and position of e-NWP NWs.

Masks

In order to build a nanoscale channel in an FET, e-NWP with a maximum speed of 1 m/s was used to print well-

Figure 10 (a) The e-NWP fabrication process of ferroelectric memory with polymer semiconducting NW. (b) SEM images of thermally-treated P3HT NW on the SiO_2 substrate. (c) $I_{\text{DS}}-V_{\text{G}}$ transfer curves of the device demonstrate current hysteresis that arises from non-volatile ferroelectric polarization of the PVDF-TrFE layer. (d) ON current and (e) ON/OFF ratios of devices with different number of polymer wires. (f) Time-dependent retention characteristics and (g) write/erase endurance cycles of I_{DS} in a polymer NW Fe-FET. (h) Retention data of ON current of NW Fe-FET before and after thermal treatment of polymer NW. Reprinted with permission from Ref. [18]. Copyright 2014, John Wiley and Sons.

aligned PVK NW as a shadow mask under the metal films [1]. The PVK NWs were printed on the substrate and coated with metal film deposited through thermal evaporation. Finally, the PVK NW was removed by ultrasonic treatment to leave nano-gap (Fig. 11). Different channel lengths can be achieved by adjusting the concentration of PVK solution. Even using small radius organic semiconductor NWs (P3HT/PEO NWs) as the channel can be achieved high carrier mobility ($9.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and low contact resistivity ($5.53 \Omega \text{ cm}$). Channels fabricated in this manner can have nanometer-scale lengths, and the length can be adjusted by the width of the NWs. Uniform channels can be obtained using the NW arrays as lithography masks.

A position-customizable and normal-temperature processable metallic NW electrode array was fabricated using aligned ONW templates (Fig. 12) [8]. First, AuCl_4^- was selectively adsorbed onto a P4VP NW surface due to the electrostatic interaction between metal-based anions and the protonated pyridyl of P4VP NW surface. Then the AuCl_4^- was reduced chemically using hydrazine hydrate vapor ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) to yield elemental Au nanoclusters or nanoparticles, which were deposited on the P4VP NW

array by coarsening. The Au nanoparticles provided nucleation sites and acted as catalysts for metal plating during the coarsening process. Consequently, an Au-plated NW array that had sufficient density was attained by electrical percolation. The resulting well-controlled thin metal sheath with polymer core has the advantages of very low resistivity of $7.5 \mu\Omega \text{ cm}$, high optical transmittance ($> 90\%$), and tolerance of bending. Compared with other lithography techniques, this approach produces nanoscale channels without high-vacuum process.

e-NWP can be used to fabricate arrays of 1D Ag NEs [9] (Fig. 13a). A highly-conductive Ti (3 nm)/Ag thin layer (100 nm) was evaporated onto SiO_2 (100 nm)/Si substrate, then a precisely-controlled mask that was composed of a PVDF-TrFE ONW array was printed onto the Ti/Ag thin layer by e-ONW printing. Various patterns of NWs were easily obtained by adjusting the e-ONW printer's parameters such as printing speed, direction and location (Fig. 13b, c, d). To increase the contact area between NW and Ag film, THF vapor was used to collapse the PVDF-TrFE NW, then the complex was annealed at 45°C . A cosolvent of NH_4OH , H_2O_2 and CH_3OH was used to chemically etch the areas of the Ti/

Figure 11 (a) Schematic illustration of an ONW after metal deposition process in e-NWP. FESEM images of cross section of an ONW (b) before, which show a perfect cylinder, and (c) after metal deposition process. (d) Corresponding grid-structured pattern of gold nano-gap (inset: region of intersection, scale bar, 200 nm). (e) Parallel array of nano-sized gold gap with 50-nm spacing. (f) Size of gold gap can be controlled by diameter of NWs. Scale bar, 100 nm (white), 500 nm (black). Reprinted with permission from Ref. [1]. Copyright 2013, Springer Nature.

Figure 12 Electroless Au plating on a NW. (a) Schematic of electroless Au plating procedure on P4VP NW. (b) Parallel pattern of Au NW array with 100-μm pitch. (c) SEM image (left) and schematic illustration (right) of a cross section of an electrolessly-plated Au NW (200 nm, scale bar). Reprinted with permission from Ref. [8]. Copyright 2017, American Chemical Society.

Figure 13 (a) Schematic illustration of the fabrication procedures of Ag NEs by printed NW lithography. SEM images of Ag NE arrays with various patterns: (b) parallel lines, (c) perpendicular grid lines, and (d) alternate straight and serpentine lines (scale bar: 300 μm). Reprinted with permission from Ref. [9]. Copyright 2017, The Royal Society of Chemistry.

Ag layer that were not protected by the NW masks. Finally, the NW masks were removed by washing with acetone. A uniformly-patterned, highly-conductive and large-scale Ag NE array was attained. Regardless of the width of the pattern, the resistivity of the Ag NE was consistent and lower than in previously-reported Ag NWs. e-NWP produces nano-scale silver NW arrays without the use of wet chemical etching.

Synaptic transistor

Synaptic transistors (STs) fabricated using e-NWP can emulate the morphology, working principles (e.g., short-term plasticity, long-term potentiation, long-term depression) and energy consumption of synaptic junctions of nerve fibers [12] (Fig. 14). In the simulation of various synaptic behaviors, symmetry between enhancement and inhibition is the most important requirement (Fig. 14j, k). The current ONW device structure can simulate the storage capacity of synapses (Fig. 14l). The positive resistances accumulate continuously toward the conduction channel, leading to a significant increase in potential by using a series of positive resistances. The accumulation of

the negative resistances also happens by using a series of negative resistance. The excitatory postsynaptic current (EPSC) of ONW device is related to the number of spikes (Fig. 14m). The process yielded transistors that had well-confined 300-nm channel length. The NWs had a core-sheath structure and were laid across a short nanochannel. The average energy consumption for each NW was ~ 1.23 fJ per spike which reached the energy consumption level of biological synapse (Fig. 14m, n). A new method was demonstrated for the manufacture of nano-neuromorphic devices which was an important advance in the development of high density and low energy consumption electronic devices.

A stretchable ONW ST (s-ONWST) based on ionic gel gated FET was used to simulate the biological synapses in the sensorimotor nerve system [4] (Fig. 15a). Negative presynaptic voltage spikes gathered anions together near the surface of ONW; these anions aggregated on the surface of ONW and induced hole transport channels, and then generated EPSC with the required driving voltage. A single presynaptic stimulus (-1 V, 120 ms) induced an EPSC of -6.43 nA, and due to the reverse

Figure 14 Process of (a) a presynaptic spike and (f) two presynaptic spikes to a postneuron and (b) a spatiotemporally correlated spike and (g) two spatiotemporally correlated spikes electrical pulses to an ONW ST that induces current responses through the ONW active channel. An EPSC of an ONW ST triggered by (c) a negative presynaptic spike and (e) two spikes. (d) Inhibitory postsynaptic current of an ONW ST triggered by a positive presynaptic spike. (h) EPSC of a single or pair of presynaptic spikes versus time. (j–m) Long-term synaptic plasticity. (n) Short-term synaptic of a nano-gap ONW ST enhancement by two negative pulses. (o) Energy consumption per synaptic event of current available synaptic devices. Reprinted with permission from Ref. [12]. Copyright 2016, American Association for the Advancement of Science.

diffusion of the anion through the electrolyte, the EPSC decayed to a resting current of $I \approx -0.2$ nA in a matter of seconds (Fig. 15b). Paired pulse stimulation (PPF) produced by continuous pulses was separated by short interval Δt to strengthen the postsynaptic signals, resulting in short-term synaptic enhancement. And the decrease of Δt enhanced the postsynaptic current. For s-ONWST artificial synapses, the second peak value of EPSC (A_2) reached 1.34 times of the first peak value of EPSC (A_1) stimulated by a paired pulse of $\Delta t = 120$ ms (Fig. 15b). This phenomenon was due to the fact that the accumulated anions produced by the first pulse had not completely diffused before the accumulation of additional anions caused by the second pulse. Therefore, EPSC increased with the increase of accumulated anions near NW. With the increase of Δt , the number of anions accumulated from the first peak gradually dissipated, so PPF (A_2/A_1) decreased. (Fig. 15c). s-ONWST still possessed various synaptic properties under 100% tensile strain, such as PPF (A_2/A_1), spike voltage-dependent plasticity (SVDP), spike number-dependent plasticity (SNDP), spike frequency-dependent plasticity (SFDP) and EPSC gain (A_{10}/A_1). According to the applied presynaptic spike voltage (-0.3 to -1 V, increment is

-0.1 V), strengthen EPSC current from -1.96 to -6.66 nA; the EPSC increase was obtained because of the adding voltage and the subsequently accumulative ion amount (Fig. 15d). As the number of presynaptic stimulates n increased from 0 to 50, EPSC increased due to the accumulation of anions (Fig. 15e). In the s-ONWST, EPSC increased steadily with the increase of frequency of presynaptic spike f_{SPIKE} (Fig. 15f). With the increase of f_{SPIKE} , EPSC gain (A_{10}/A_1) strengthened from 1.07 to 1.55 slowly, in consistence with the dynamic high-pass filtering of signal transmission in synapses (Fig. 15g) [4]. In this work, the first neurologically-inspired organic optoelectronic sensorimotor synapse by e-NWP showed stable I - V characteristics and various typical postsynaptic behaviors. An artificial muscle was actuated by the organic optoelectronic sensorimotor synapse with the biological muscle tension responses during contraction. This suggests that an artificial sensorimotor nervous system of soft electronics and neurorobotics can be fabricated using e-NWP.

CONCLUSION AND PERSPECTIVE

e-NWP to prepare NW materials has become an important academic and technical topic in the field of ma-

Figure 15 (a) Neural signal transmission from pre-neuron to postneuron through a biological synapse (left) and an artificial synapse (right). (b) EPSCs triggered by single and double spikes. A_1 and A_2 are EPSCs of the first and second spikes with an interval of 120 ms, respectively. (c–g) Postsynaptic characteristics of stretched artificial synapse from 0 to 100% strains; (c) the function between PPF (A_2/A_1) and interval, (d) SVDP with various gate voltages, (e) SNDP. SFDP characteristics with spike frequency, (f) maximum EPSCs and (g) EPSC gain (A_{10}/A_1) of stretched artificial synapse. Reprinted with permission from Ref. [4]. Copyright 2018, American Association for the Advancement of Science.

materials science and technology. e-NWP has advantageous properties such as simple manufacturing, low cost, and precision control, so the method has become an important technique for preparation of NWs materials. e-NWP has been used to prepare a wide variety of NWs,

including polymers, metal-oxide-doped and metal-doped NWs. However, the preparation of NWs by using e-NWP still has limitations.

First, e-NWP has demonstrated its feasibility in printing polymeric and metallic NWs using several re-

presentative materials. These are just initial attempts, and the research field is still at its beginning stage. More functions can be potentially realized by this approach. For example, light, magnetic field, and thermal responsive materials can be blended into the NWs or directly printed into NWs to realize different functionalities. We can also use flexible stretchable materials, or biomedical materials to fabricate NWs for flexible electronics or biomedical applications.

Second, molecular structures of the source material and their nanoscale aggregation behaviors in NW could significantly influence the electrical or optical properties of the printed NWs. However, these correlations still require further investigation.

Furthermore, e-NWP has been feasible to print semiconductor lines, conductor lines, insulator lines, etc., and these components are essential for constructing integrated circuits. All-NW electronics can be expected using this technique for future applications such as wearable electronics.

NWs have potential applications in highly-integrated optoelectronic devices, microfluidic chips, soft bionics, flexible wearable electronic NWs textiles, software robots, biological monitoring, aerospace equipment, and other fields. Therefore, solving the above three scientific problems will promote the development of modern science and technology.

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Conflict of interest The authors declare that they have no conflict of interest.

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数码可控纳米线打印的最新进展

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摘要 数码可控纳米线打印(e-NWP)技术可用于制备高精度印刷图案化的纳米线。该技术将有望促进大面积图案化纳米线阵列、高精度和高集成度器件、纳米机电系统和生物启发器件等领域的发展。e-NWP打印器件的电学特性可以通过控制纳米线的间隙和直径来调节。这种技术已被应用于场效应晶体管、神经拟态器件和掩模板等。本综述总结了e-NWP的基本原理、材料选择、打印方法和应用尝试,并展望了在拓展e-NWP应用和商业化进程中仍需解决的问题。