A New 'Sticking' Coating Method for the in Situ Formation of Nanofiber Networks on Micrometer to Millimeter-Sized Surfaces

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Experimental section.

Materials: PVDF-*co*-HFP ((-CH₂CF₂-)_m[-CF₂CF(CF₃)-]_n, M_w ~400,000, M_n ~130,000, m/n = 10:1 (molar ratio)), PVA ((-CH₂CHOH-)₁₅₀₀), PAN ((-CH₂CHOH-)_n, M_w ~150,000) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetone (CH₃COCH₃) and N,N-dimethylformamide ((CH₃)₂NCHO) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Ultrapure water was obtained using an Aquarius GS-500 (CPW, Advantec Co., Saijo, Japan). Aluminum plate and PET sheet were commercially available. Porous PETs were obtained using circle cutter.

Cocktail preparation: PVDF-HFP was dissolved in acetone (unless indicated otherwise, 20% w/w was used. In the experiment shown in Figure 2, we varied the concentration) by stirring for 24 h at 60 °C. The PVA was dissolved in ultrapure water (10% w/w) by stirring for 24 h at room temperature. The PAN was dissolved in N,N-dimethylformamide (10% w/w) by stirring for 24 h at room temperature.

Electrospinning conditions: Cocktails were loaded into a plastic syringe with needles. The vertical tip-to-collector distance between the tip of the nozzle and the collector was 20 cm. The nozzle direction was set onto a center of the collector. The applied voltage was set at 20 kV by a high voltage power unit. The flux of the syringe pump was set at 1 mL/h. The electrospinning time was 30 min.

Characterization: The morphology of the samples was characterized using a digital microscope (VH-Z500R, KEYENCE, Japan). For endoscope application, a rigid lens-scope with 4 mm diameter and 0° viewing directions were used in the high definition video system (EndoArm, Olympus Co., Tokyo, Japan)



Figure S1. Scanning electron microscopy images of polyvinyl alcohol nanofiber (left) and polyacrylonitrile (right) fabricated on porous PET with 20 mm pores.



Figure S2. Photographic images showing the influence of the sticking speed on the elastic moduli of the fiber sheet. The quantified elastic moduli analysis is reported in our previous work (see REF S1).

Note S1 Detailed analysis of the possible fiber formation mechanism

In general, the electrospun polymer states after normal electrospinning are divided into 3 types: ^{S2,S3} (i) Polymer particles are deposited on a collector on which the electric repulsion force ($F_{repulsion}$) outweighs polymer cohesion ($F_{cohesion}$); (ii) branched fibers are deposited if $F_{cohesion}$ > F_{repulsion}; and (iii) fibers adhere on a collector in a spiral orbital owing to ionic wind when F_{cohesion} is strong enough to prevent fiber splitting by F_{repulsion}, as shown in Figure S3A. Thus, we carefully observed which deposition coating state (F1-F3) contributed to the polymer state (i)-(iii) by observing the fiber (or particle) morphologies, as shown in Figure S4A-E. The fiber deposition can be categorized into five states: (1) particle deposited with the F1 state (PF1, Figure S4A); (2) branched fiber deposited with the F1 state (BF1, Figure S4B); (3) branched fiber deposited with the F2 state (BF2, Figure S4C); spiral fiber deposited with the F2 state (SF2, Figure S3D); and (5) spiral fiber deposited with the F3 state (SF3, Figure S4E), as summarized in the schematic diagram in Figure 3B. The factor that distinguish between the BF1 and BF2 sates is the pore size of the PET because the terminal parts of the branched fiber are widely distributed, which has a strong influence on the pore sizes. The factor that determines the SF2 and SF3 state is the fiber stiffness. When the spiral fibers are deposited on the patterned collector, the widely swayed fibers are drawn by various pore areas. Thus, the fiber adheres on the collector to bridge the pores. However, the thinner fibers are not strong enough to brace the pores and form the SF2 state. The fiber stiffness is determined not only by the fiber diameter but also by the polymer chemistry. As shown in Figure S1, polyvinyl alcohol nanofibers contributed to a SF3 state even though the fiber diameters were much smaller than that of PVDF-HFP because the polarity and hydrogen bonding by the hydroxy group improved the strength of the fiber.



Figure S3. Analysis of the possible electrospun polymer states on the patterned surface. (A–B) Schematic illustrations of the possible polymer states during electrospinning. As the polymer condensation varied, i) particles, ii) branched fibers, or iii) spiral fibers polymer states were obtained, which depended on the balance between the polymer cohesion ($F_{cohesion}$) and electric repulsion force ($F_{repulsion}$). (B) Possible correlation between the polymer states (i)–(iii) with the deposition states (F1–F3); the coating behavior of F1 appears with the particle state (PF1) and branched fiber state (BF1). Branched fibers deposited on a patterned surface with the F2 state (BF2) also appear. Spiral fiber with F2 or F3 states appeared as SF2 and SF3, respectively.

A PF1	B BF1	C BF2	D SF2	E SF3
Pore area	Pore area	Pore area	Pore area	Pore area
		PETaroa		Spiral fibers
PET area	PET area		PET area	PET area
Al area	Al area	Al area	Al area	Al area Scratch damage
		AND AND THE		Uncoated Al'area
Parilalo	Branched fibers	Branched fibers	Spiral fibers	Spirel fibers
Only on Al area	Only on Al area	On AI & PET area	On AI & PET area	On Pore & PET area
				Scale bar: 50µm

Figure S4. Optical images to support the categorization of Figure S3: (A) PF1, (B) BF1, (C) BF2, (D) SF2, and (E) SF3 on the pore, PET, and Al area.

Note S2 Simulation conditions and results

The simulation of the electric field distribution on a porous PET surface based on finite elemental method was carried out by using commercial software (CST STUDIO SUITE, Dassault Systems France). To design a simulation model of electrospinning, a porous PET film (size: $160 \times 160 \times 0.18$ mm, pore: 10-20 mm of 5×5 pores with the same intervals) attached to an aluminum array (size: $160 \times 160 \times 9.0$ mm, array width: 9.0 mm), which is used as a collector, was placed 200 mm away from a syringe tip (at (x, y)=0) composed of a cylinder (diameter: 0.8 mm). Then, the electric field distribution was calculated by a solver while a voltage of 20 kV was applied between the syringe tip and the collector. The electrofield distribution with different pore sizes is shown in **Figure S5**. By changing the diameter of the pore, the electrofield distribution also varied. **Figure S6** shows the electric field vector mappings with different pore sizes. The macro electrofield vector does not influence the pore size.



Figure S5. (A) Simulation of the z-direction electric field distribution on porous PET with different pore sizes (10 mm, 15 mm, and 20 mm). (B) The distribution graphs with different pore sizes (10 mm, 15 mm, and 20 mm) as a function of y at x=0 (a pore center) by the finite element method.



Figure S6. Electric field vector mappings at x=0 (a center of the simulation models) for porous PET with different pore sizes (10 mm, 15 mm, and 20 mm).

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