

1 **Supporting information**

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3 **Proton exchange membrane fabricated from chemically heterogeneous nonwoven with**  
4 **sandwich structure by the program-controlled co-electrospinning process**

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11 **EXPERIMENTAL SECTION**

12 **Materials.** The SPFEK polymer used was obtained from the scale up production line of our laboratory, and  
13 the synthesis procedure has been published earlier<sup>1</sup>. The structure of SPFEK is depicted in Fig. 1e.  
14 poly(diallyldimethyl ammonium chloride) (PDDA, 20 wt% in water, molecular weight 100,000~200,000)  
15 and poly(styrene sulfonic acid, sodium salt) (PSS, molecular weight 500,000) was purchased from Alfa  
16 Aesar. Nafion 117 was supplied by DuPont chemical. Poly(ether sulfone) (PES) was purchased from Tianjin  
17 Shengtai chemical Plant, China. N,N-dimethylacetamide (DMAc), Hydrochloric acid, Sodium chloride,  
18 Ferrous sulfate heptahydrate, Sulfuric acid (95–97 %) and Hydrogen peroxide (30 wt%) were obtained from  
19 commercial sources.

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21 **Fabrication of Chemically Heterogeneous Nonwoven composed of bead-free SPFEK nanofiber and**  
22 **beaded PES nanofiber.** The schematic of the custom-built electrospinning apparatus used to prepare  
23 nanofibrous nonwoven is shown in Fig. S1. The two needles were fixed on the same metal electrode to  
24 ensure that the same voltages were applied during the co-electrospinning process. A nonwoven contained  
25 both SPFEK nanofibers and PES nanofibers obtained on the collector by moving the metal electrode back  
26 and forth along a horizontal axis. The typical electrospinning parameters were as follows: 30% (w/v) SPFEK  
27 (IEC of 1.45 mmol/g) solution in DMAc and 20% (w/v) PES solution in DMAc were loaded into syringe A  
28 and syringe B, respectively. A voltage of 30 KV was applied between the metal electrode and the grounded  
29 collector. The distance between the two needles was fixed at 1 cm, the metal electrode moved back and forth  
30 at a speed of 1 mm/s along a horizontal axis 80 mm in length. A grounded aluminum plate (5 cm×9 cm)

31 served as the collector. The needle-to-collector distance was 18cm. A syringe pump was used to squeeze out  
32 the polymer solutions through the needles (inner diameter 0.45 mm). The duration of electrospinning process  
33 was 5h, and the squeezing speeds of the two polymer solution were program-controlled independently. For  
34 the first two hours, only SPFEK solution was squeezing out and its squeezing speed was fixed at 0.18 ml/h  
35 for the whole 5h. For the third hour, PES solution was co-electrospun as well as SPFEK solution, and the  
36 speed of PES solution was controlled at 0.09 mL/h. For the last 2h, PES solution was stopped squeezing out  
37 and only SPFEK solution was kept squeezing out to finish the electrospinning process. A bench-top  
38 hydraulic press was employed to preliminarily compact the chemically heterogeneous sandwiched nonwoven  
39 with a pressure of 10MPa at room temperature. The nonwoven was compacted with thickness reduced from  
40 300 to 130  $\mu\text{m}$  in 2 minutes. Fig. S2 shows the surface appearance of the nonwoven after compaction.

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42 The LBL self-assembly of PDDA-PSS multilayer was carried out by alternate dipping of the pre-compacted  
43 nonwoven in PDDA (10mM) and PSS (10mM) solutions at room temperature for 10 minutes. After each  
44 dipping step, the nonwoven was washed with deionized water. The LBL self-assembly nonwoven with five  
45 PDDA-PSS bilayers was finally washed with deionized water, followed by protonation treatment in 0.5 M  
46  $\text{H}_2\text{SO}_4$  at 80  $^\circ\text{C}$  for 1 h, then washed again with deionized water and dried at 110  $^\circ\text{C}$  for 2 h.

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48 At last, the nonwoven was immersed in mixture solvent of DMAc and water ( $V_{\text{DMAc}} : V_{\text{water}} = 10 : 90$ ) at  
49 room temperature for 3 minutes, wiped excess solvent on surface with filter paper, then compacted under a  
50 pressure of 1 MPa at 100  $^\circ\text{C}$  for 3 h when the nonwoven was surrounded by four pieces of solid paper in 110  
51  $\mu\text{m}$  thickness as shown in Fig S4. The resulting yellowish transparent F-SPFEK membrane in a thickness of  
52 110  $\mu\text{m}$  was further dried in a vacuum oven at 110  $^\circ\text{C}$  for 10 h, immersed in 0.5 M  $\text{H}_2\text{SO}_4$  at 80  $^\circ\text{C}$  for 1 h,  
53 then washed and stored in deionized water.

54

55 **Membrane characterization.** F-SPFEK membrane was characterized in terms of ionic exchange capacity  
56 (IEC), water uptake, swelling ratio, mechanical strength, oxidative stability, proton conductivity and fuel cell  
57 performance. Measurements were also conducted on pretreated Nafion 115 (immersing for 30min at 80 $^\circ\text{C}$   
58 each in 5 wt%  $\text{H}_2\text{O}_2$ , deionized water and 8 wt%  $\text{H}_2\text{SO}_4$ ) and a homogeneous SPFEK membrane (IEC,  
59 1.45mmol/g) with a thickness of 120 $\mu\text{m}$  cast directly from 10 wt% SPFEK solution in DMAc (dried at 80 $^\circ\text{C}$   
60 for 24 h in hot air circulation oven and further dried at 110 $^\circ\text{C}$  for another 10 h in vacuum oven).

61 The IEC of the membranes were determined by traditional titration using NaOH solution. The water uptake  
62 measurements were conducted by measuring the weight differences between fully hydrated membranes and  
63 vacuum dried membranes. The dry membranes were obtained under vacuum at 110 °C for 10 h. The water  
64 uptake was calculated according to the following Eq. 1:

$$65 \quad \text{Water uptake (\%)} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100\% \quad (\text{Eq. 1})$$

66 Here,  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are weights of the fully hydrated and dry membranes, respectively.

67

68 Mechanical tensile strength was determined at 30 °C and 100% relative humidity by a universal test machine  
69 (Model: SANS-CMT, Shenzhen, China). The cross-head speed was set at 2 mm/min. The samples were  
70 prepared by cutting them into a dumbbell shape. Oxidative stabilities were investigated by immersing the  
71 membrane samples in Fenton's reagent (2ppm FeSO<sub>4</sub> in 3 wt% H<sub>2</sub>O<sub>2</sub>) at 80 °C for 1 h. The stabilities were  
72 evaluated by the reduction in mass. Proton conductivity measurements were performed using a Solartron  
73 electrochemical interface 1287 and 1255B instrument over the frequency range from 1 MHz to 100 Hz.  
74 Specimens of the membranes were soaked in deionized water for 24 h prior to the test. Each specimen was  
75 clamped between two gold electrodes and placed above liquid water in a thermocontrolled humidity chamber.  
76 Equilibration time at each temperature was fixed at 0.5 h.

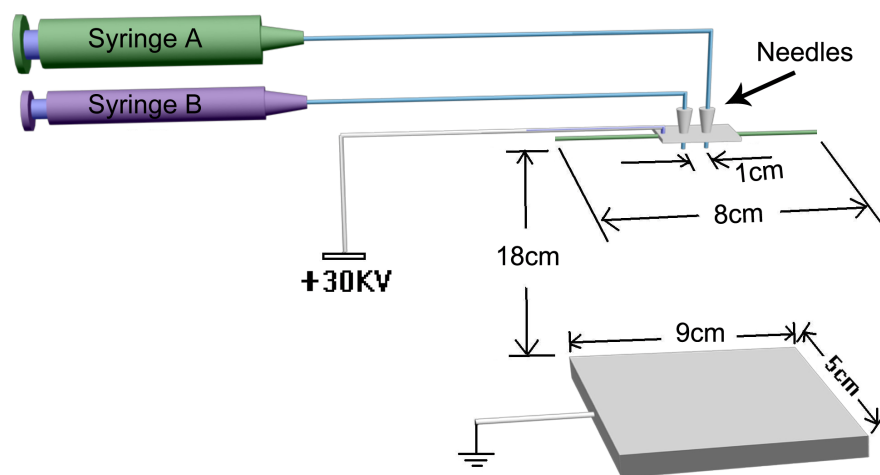
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78 A membrane-electrode assembly (MEA) with 4 cm<sup>2</sup> active area was used in the fuel cell tests. A single  
79 PEMFC cell was operated at 80°C in humidified H<sub>2</sub> and O<sub>2</sub> gases with no gas back-pressure. The  
80 polarization curves were measured using a fuel cell test station (Arbin Instruments, 160269). The power  
81 densities were calculated from the steady-state voltages and applied currents.

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### 83 **Notes and references**

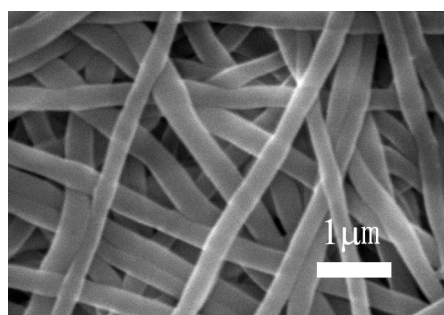
84 1 Y.L. Chen, Y.Z. Meng, S.J. Wang, S.H. Tian, Y. Chen and A. S. Hay. *J. Membr. Sci.*, 2006, **280**, 433



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86 **Fig. S1** Schematic of the custom-built electrospinning apparatus for preparation of chemically heterogeneous sandwiched  
87 nonwoven

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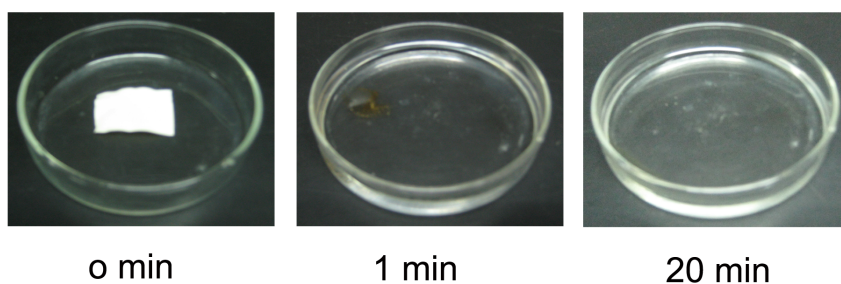


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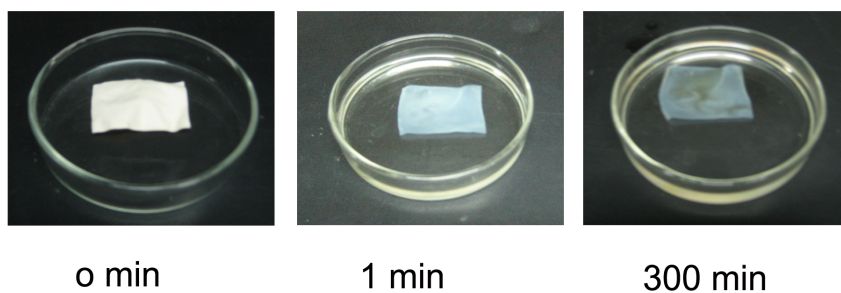
90 **Fig. S2** SEM image of nonwoven after pre-compaction

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(a) SPFEK fibrous nonwoven



(b) SPFEK fibrous nonwoven after LBL self-assembly

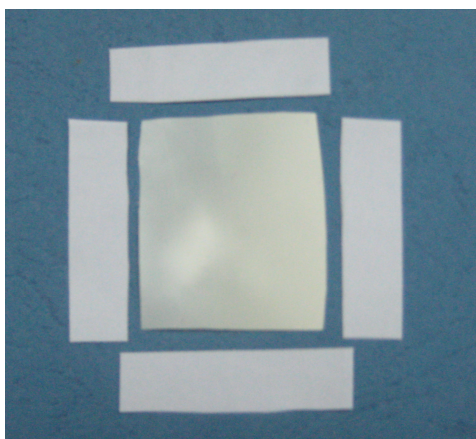


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93 **Fig. S3** Solubility of nonwovens before and after LBL self-assembly in DMAc at 100°C



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96 **Fig. S4** Nonwoven surrounded by four pieces of solid paper (110 $\mu$ m in thick).