Electronic Supplementary Information

Environmentally Benign Modification of Breathable Nanofibrous Membranes Exhibiting Superior Waterproof and Photocatalytic Self-cleaning Properties

Jing Zhao,[abc] Weixia Zhu,[ac] Xianfeng Wang,*[abc] Lifang Liu,[ac] Jianyong Yu,[c] and Bin Ding*[ac]

[a] *State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Textiles, Donghua University, Shanghai 201620, China.*

E-mail: binding@dhu.edu.cn, wxf@dhu.edu.cn; Fax: +86 21 62378202.

[b] *Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China.*

[c] *Innovation Center for Textile Science and Technology, Donghua University, Shanghai 200051, China*

Experimental details

1. Materials

PAN powders (Mw=90 000 g mol^{-1}) was purchased from Co., Ltd., Japan. ZnO NPs dispersion with washing resistance was bought from Daxinong nanotechnology Co. Ltd. *N,N*-dimethylacetamide (DMAc) and ethanol were supplied by Shanghai Chemical Reagent Co. Ltd. 3M Scotchgard® C4 waterborne water repellent (PM3635) was obtained from 3M Co. Ltd. Methylene blue (MB) was got from Aladdin Chemical Reagent Co. Ltd. All chemicals were employed without any further treatment.

2. Preparation of PAN NFM

4.5 g PAN powder was added into 45.5 g DMAc solution with stirring for 12 h to make PAN solution. PAN membranes were manufactured using a DXE-2 electrospinning machine (SOF Nanotechnology Co. Ltd., China) with temperature of 25 ±2 °C and relative humidity of 45 ± 2%. The applied voltage was 30 kV, the feed rate was 1 mL h^{-1}, and the distance from pinpoint to the collector was 24 cm.

3. Characterization

The microstructures of prepared fibrous membranes were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The water contact angle (WCA) was measured by contact angle goniometer (Kino SL200B, USA). The element content of the fiber surface was tested by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi XPS system (Thermo Fisher Scientific Inc., USA). The porous structure of the membranes was analyzed by the capillary flow porometer (CFP-1100AI, Porous Materials Inc., USA). The porosity of the membranes was calculated using the same method as before.[1-3] The thickness was detected by a thickness gauge (CHY-C2, Labthink Instruments Co. Ltd., China). Energy dispersive X-ray spectroscopy (EDX) was employed to study the microstructure and composition of the corresponding fibrous membranes.

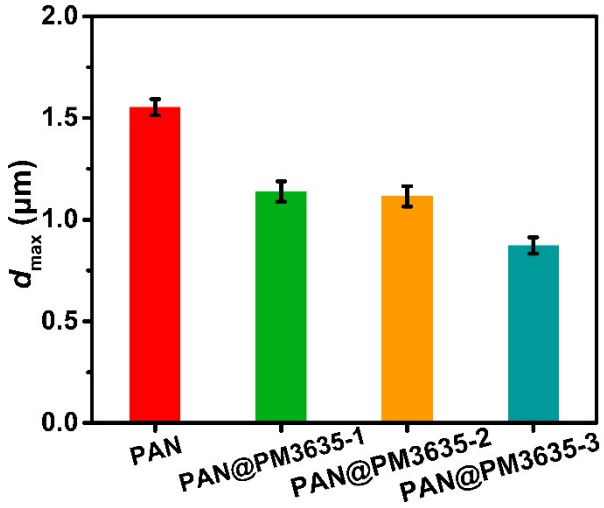

Fig. S1 d_{max} of PAN@PM3635 NFM fabricated from various concentrations of PM3635.

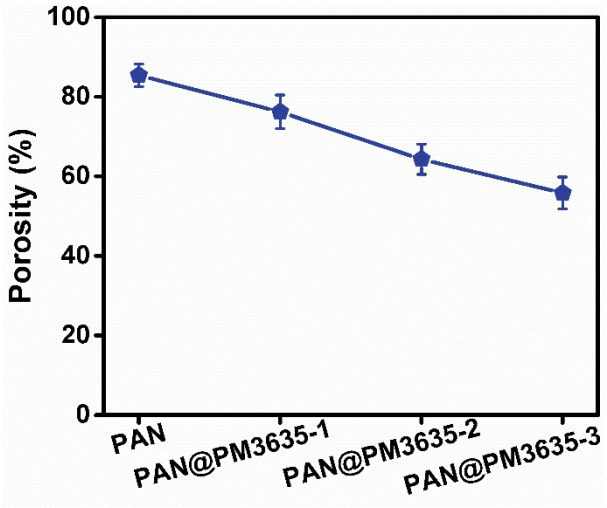

Fig. S2 Porosity of PAN@PM3635 NFM with different PM3635 concentrations.

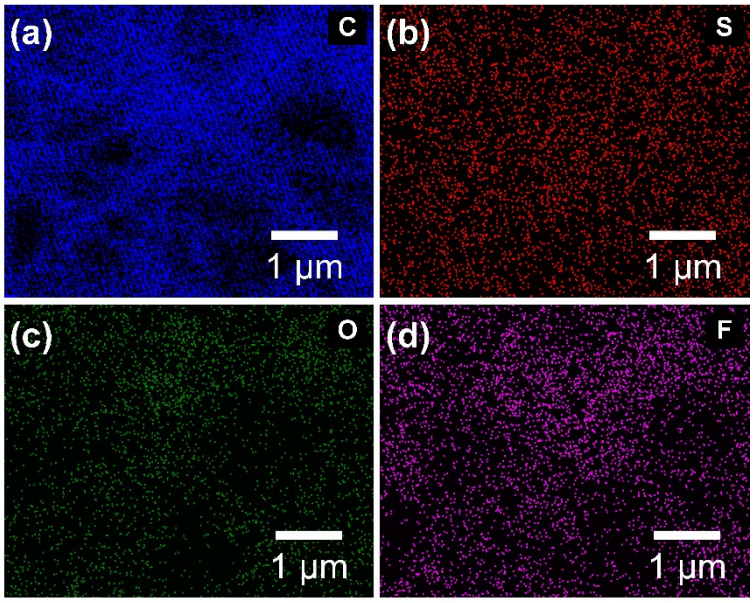

Fig. S3 Elemental mapping images of C, S, O, and F of PAN@PM3635-2/ZnO-3 NFM.

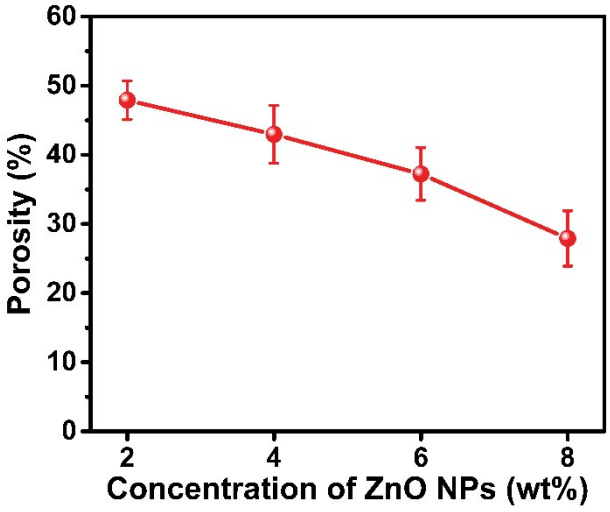

Fig. S4 Porosity of PAN@PM3635-2/ZnO NFM with different concentrations of ZnO NPs.

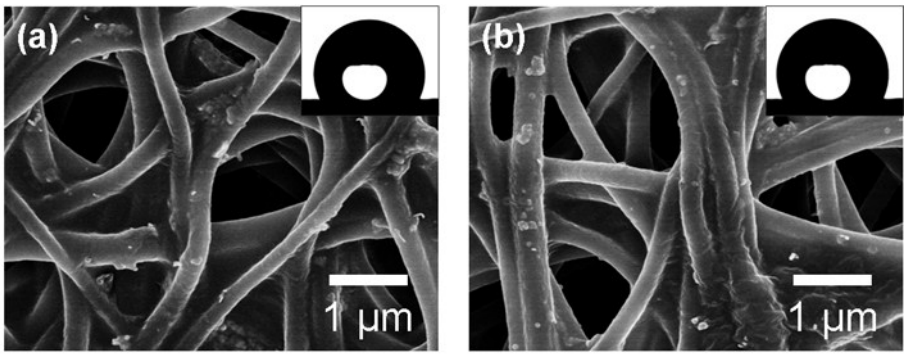

Fig. S5 Under-water stability of PAN@PM3635-2/ZnO-3 NFM.

PAN@PM3635-2/ZnO-3 NFM was dipped in water/ethanol mixture for ultrasonic treatment[4] to investigate the stability in under-water conditions, after 12 h, the morphology and water contact angle (WCA) of the membranes were tested. As shown in Fig. S5a, the rough structure of ZnO NPs on the surface of the initial PAN@PM3635-2/ZnO-3 fibers could be seen clearly, and the water contact angle was 116.6°. The morphology of the fibers after ultrasonic treatment was displayed in Fig. S5b, no obvious changes could be observed, and the WCA remained almost the same (114.9°), indicating good stability of PAN@PM3635-2/ZnO-3 NFM in under-water conditions.

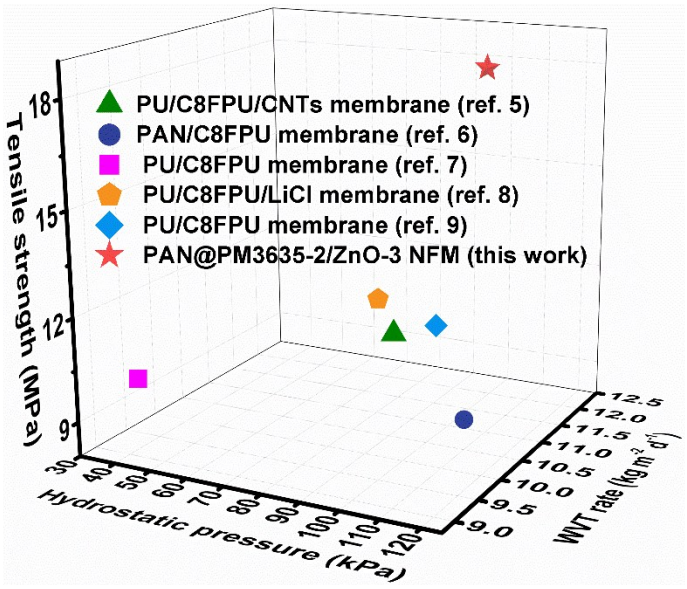

Fig. S6 Comparison of comprehensive properties among PAN@PM3635-2/ZnO-3 NFM and fibrous membranes containing long perfluoroalkyl chain.

For PU/C8FPU/CNTs membrane containing long perfluorooctyl chain (R_{fn}, n=8, denominated as C8FPU), it displayed high hydrostatic pressure (108 kPa), but low WVT rate (9.2 kg m^{-2} d^{-1}) and medium tensile strength (12.5 MPa).[5] In terms of PAN/C8FPU membrane, it exhibited the best

waterproofness with a hydrostatic pressure of 114 kPa, however, its WVT rate was only 10.1 kg m^{-2} d^{-1}, and tensile strength was just 9.4 MPa.[6] For PU/C8FPU fibrous membrane, it exhibited a low hydrostatic pressure of 39.3 kPa, the WVT rate was 9.2 kg m^{-2} d^{-1}, and tensile strength was 11.6 MPa.[7] With respect to PU/C8FPU/LiCl fibrous membrane, the hydrostatic pressure was 82.1 kPa, WVT rate was 10.9 kg m^{-2} d^{-1}, and tensile strength was 11.6 MPa.[8] In terms of PU/C8FPU fibrous membrane, the hydrostatic pressure was 86 kPa, WVT rate was 11.9 kg m^{-2} d^{-1}, and tensile strength was 10 MPa.[9] While for PAN@PM3635-2/ZnO-3 NFM containing short fluorinated chain (R_{fn}, n=4) in this work, its hydrostatic pressure was 98.7 kPa, WVT rate was 12.0 kg m^{-2} d^{-1}, and tensile strength was 17.9 MPa.

On the whole, compared with the membranes containing long perfluoroalkyl chain, PAN@PM3635-2/ZnO-3 NFM with better eco-friendliness and higher security exhibited comparable comprehensive properties.

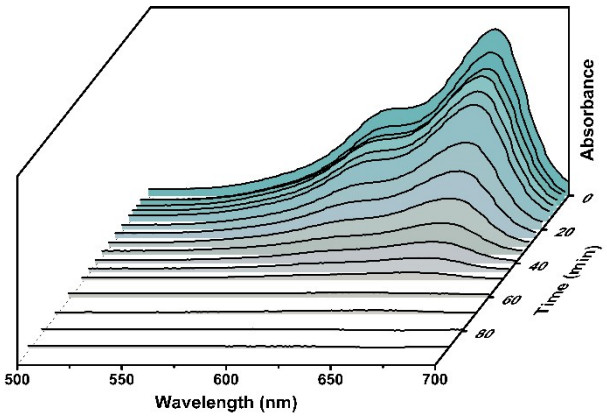

Fig. S7 Absorption spectra of MB dye of PAN@PM3635-2/ZnO-2 NFM under UV irradiation for different time.

Table S1. XPS data of PAN@PM3635 membranes with various concentrations of PM3635.

Sample	F%	C%	N%	O%	S%	F/C
PAN		76.52	20.55	2.94		
PAN@PM3635-1	22.74	55.10	4.86	14.81	2.49	0.413
PAN@PM3635-2	28.08	49.45	4.35	15.38	2.74	0.568
PAN@PM3635-3	23.83	52.05	5.21	16.24	2.68	0.458

Table S2. Typical EDX results of PAN@PM3635-2/ZnO-3 NFM.

Elment	Weight%	Atomic%
C	56.25	71.20
Zn	18.36	4.27
F	4.28	3.43
O	4.66	4.42
N	14.54	15.78
S	1.90	0.90
Total	100.00	100.00

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