Electronic Supporting Information

One-step nano-topography construction by polyaniline polymerization for superhydrophobic nanofibrous membrane towards direct contact membrane distillation

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S1 Schematic of homemade LEP instrument

The LEP of the memebrane is defined as the pressure when three drops of water fall.



Fig. S1 Schematic of homemade LEP instrument.



S2 Schematic of the laboratory-scale DCMD system

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S3 UV-vis spectrum of PANi@PVDF NFM.

The UV-vis spectrum shows that the polyaniline is formed on membrane surface after polymerization. Generally, there are two absorption bands of the eigenstate

polyaniline at 320 and 620 nm corresponding to benzenoid and quinonoid structures. However, the absorption peak at 620 nm is red-shifted by up to 30 nm due to the doped with hydrochloric acid. The red shift indicates that the protonic acid is doped on the quinonoid structures.



Fig. S3 UV-vis spectrum of PANi@PVDF NFM.

S4 Hydrophobization mechanism analysis

The mixture of PDMS precursor has a high viscosity (CP: 3900), which can be cured to a tough and transparent elastomer after treating at a high temperature. This process is similar to applying glue to a substrate and eventually curing into a transparent elastomer. Therefore, PDMS could be adhered and cured to the PANi@PVDF substrate. FTIR spectra can prove that PDMS has cured to the PANi@PVDF substrate (Fig. 2h).

The chemical structural formula of 17-FAS is shown in the Fig. S4 (a). After heat treatment, the basic component and the curing agent crosslink to form a polymer network of PDMS. Moreover, this polymer network generally exhibits a dense and non-porous structure as shown in Fig. S4 (b) (We fabricated a PDMS membrane under the same reaction condition to demonstrate the dense structure). It is well known that, both PDMS and 17-FAS are hydrophobic, thereby the two hydrophobic macromolecules can be combined by attractive hydrophobic interactions. In addition, the 17-FAS with long molecular chain could also be embedded in the dense PDMS matrix due to steric effects after the curing process. The EDS analysis (Fig. 2i) shows that the elemental fraction of fluorine atoms increased significantly after hydrophobization, demonstrating the 17-FAS was successfully modified on the membrane surface.

The surface energies of $-CF_3$, $-CF_2$ -, $-CH_3$ and $-CH_2$ - groups are 6, 18, 24, and 31 mN/m, respectively. The PDMS surface is occupied by the $-CH_3$ group, while the 17-FAS surface is occupied by $-CF_3$ and $-CF_2$ -. Consequently, the membrane surface containing 17-FAS will have lower membrane surface energy.



Fig. S4 (a) The curing reaction and the chemical structural formula of 17-FAS and the Part-A of Sylgard186. (b) The silane chemistry between 17-FAS and polydimethylsiloxane. (c) The SEM micrograph of polydimethylsiloxane membrane.

S5 AFM image of F/Si-PANi@PVDF nanofiber



Fig. S5 The AFM image of F/Si-PANi@PVDF nanofiber. The range of the scanned area was 800 nm×800 nm.

S6 The optical photos of sliding angle

The sliding angle was measured using a continuous measurement mode of contact angle goniometer (KINO SL200B3). When the slope reached 7°, the liquid could roll on the membrane surface as shown in figure below.



Fig. S6 The sliding angle of modified F/Si-PANi@PVDF NFM.

S7 MD performance of commercial membrane



Fig. S7 The DCMD performance of the commercial PVDF membrane and F/Si-PANi@PVDF NFM in 30-hour uninterrupted operation with a temperature difference of 45 °C, feed-side salinity of 3.5 wt%.

S8 SEM image of membrane structure

Compared with commercial phase inversion membrane, electrospun nanofibrous membrane exhibits high porosity, superfine fiber and open-cell pore structure, which is beneficial for passing steam during MD application. This is the mainly reason why electrospun PVDF, F/Si-PVDF, and F/Si-PANi@PVDF NFMs have larger water flux than Millipore PVDF phase inversion membrane.



Fig. S8 SEM images of commercial Millipore PVDF membrane (phase inversion membrane), electrospun PVDF NFM, electrospun F/Si-PVDF NFM, and electrospun F/Si-PANi@PVDF NFM.

S9 Anti-fouling performance of commercial PVDF membrane

As show in Fig. S9 (a), water flux of commercial membrane has a slightly reduced when processing feed solutions containing different contaminants. SEM was used to analyze whether the membrane surface was contaminated. Fig. S9 (b) shows that there are no obvious contaminations in the treated MeB, HA, and SDBS membranes. However, significant scaling fouling was found on the membrane surface treated with colloidal silica, but this phenomenon does not exist in F/Si-PANi@PVDF NFM. This indicates that the superhydrophobic membrane is significantly more resistant to inorganic particle contamination than ordinary hydrophobic membranes owing to the self-cleaning function of superhydrophobic surface.



Fig. S9 (a) Effect of feed solutions with different kinds of contaminants on DCMD with commercial PVDF membrane. (b) SEM images of the commercial membranes after running in saline water containing methyl blue (MeB), sodium dodecylbenzenesulfonate (SDBS), humic acid (HA), and colloidal silica (Si).

S10 Coating polyaniline layers on different substrate

As shown in Fig S10, the color of all substrates eventually turn atrovirens, demonstrating that polyaniline layers can be coated on different substrates. Obviously, aniline could polymerize more evenly on tightness membrane surfaces such as commercial PVDF membrane and PI NFM compared with looseness membrane surface such as silica nanofibrous membrane according to the color distribution. In fact, the polymerization of aniline on the fibers is even. The unevenness is not caused by polyaniline, but rather the disordered orientation of the substrate itself results in an uneven visual effect. It is worth mentioning that the looseness membranes are not suitable for membrane distillation, because the water pressure will immediately deform the membrane pore leading to water passing. Contact angle pictures show that the hydrophobic properties of the membranes with polyaniline layers after hydrophobization modification are significantly improved, especially silica membrane.



Fig. S10 Coating polyaniline layers on different substrate: (a) commercial PVDF membrane; (b) silica NFM; (c) polyimide (PI) NFM.