

## Supporting Information

### Confining Nano-Fe<sub>3</sub>O<sub>4</sub> in Superhydrophilic Membrane Skin Layer to Minimize Internal Fouling

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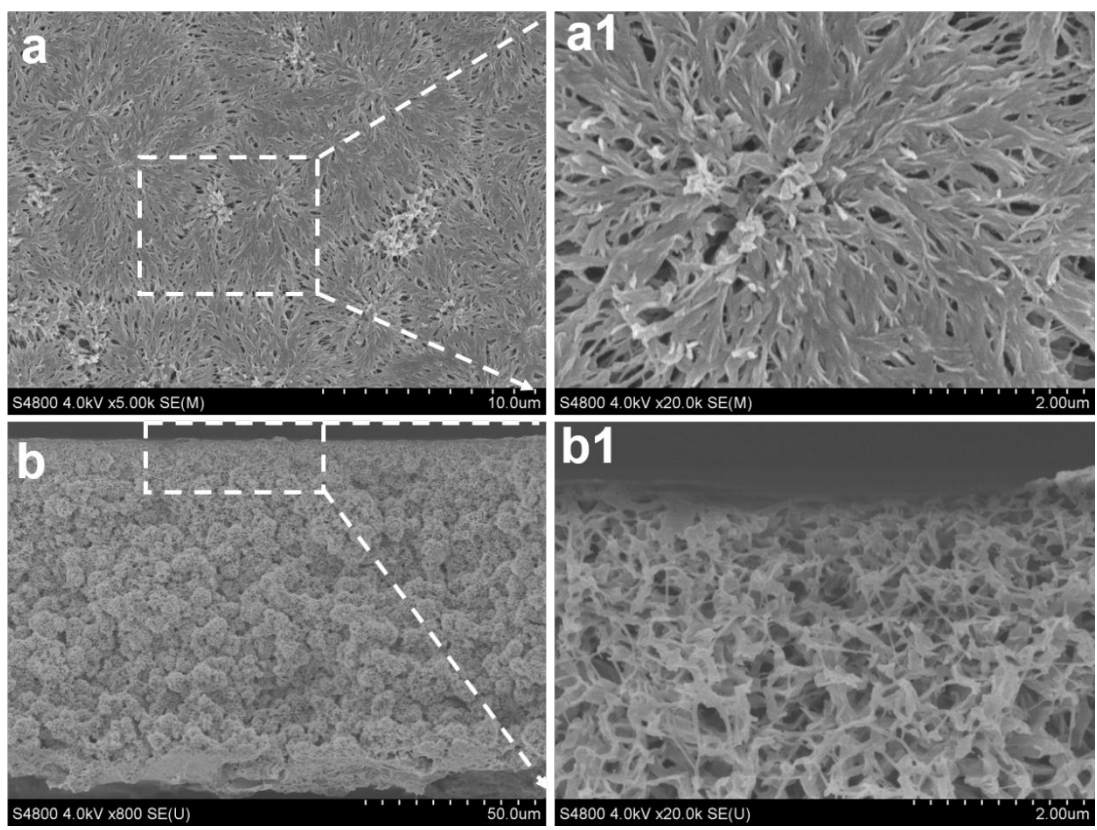
**Fabrication of the pristine PVDF membrane:** 15 g PVDF (Kynar 761-A, Arkema) is dissolved in 85 g triethyl phosphate (TEP) at 80 °C for 24 h under 300 rpm mechanical stirring. After that, the solution was deaerated under reduced pressure and then heated to 80 °C to obtain uniform PVDF casting solution. Accomplished by that, the above PVDF solution was spread onto the special PET non-woven fabric (NWF) ( $90 \text{ g}\cdot\text{m}^{-2}$ ) by a casting knife with the thickness of 200  $\mu\text{m}$ . The nascent membrane was immediately immersed into coagulation bath composed of TEP/water mixture (v/v: 5/5) for 5 s, and then moved to pure water bath at room temperature. After total solidification, the membrane was transferred to the fresh deionized water for 24 h, and dried in the air to obtain the NWF supported PVDF membrane.

**Fabrication of the P-PVDF membrane:** Pre-polymer P(VPVTES) was first synthesized via free radical polymerization as follows: 6.5 g monomers composed of NVP and VTES with molar ratio of 7/3 were added into the 100 g TEP followed by the addition of 0.08 g AIBN dissolved in 2.5 g TEP. The polymerization was carried out at 80 °C with vigorous stirring under a nitrogen atmosphere for 18 h to obtain the P(VP-VTES)/TEP solution. Subsequently, the P(VP-VTES)/TEP solution was diluted by the same weight of pure water. After that, the dried pristine PVDF porous membranes were fully immersed into the P(VP-VTES)/TEP/water solution for 2 h. Lastly, the pretreated PVDF membranes were transferred into fresh water bath at 60 °C for 24 h for a hydrothermal treatment to boost the surface crosslinking. In order to remove the residue monomer and homopolymers without crosslinking, the modified PVDF membranes were washed five times by flush water. The so modified PVDF membranes were

accordingly marked as P-PVDF. All membranes were dried at room temperature for 48 h for further characterization.

**Table S1.** The element mass fraction on Fe<sub>3</sub>O<sub>4</sub>@P-PVDF and P-PVDF membrane surfaces.

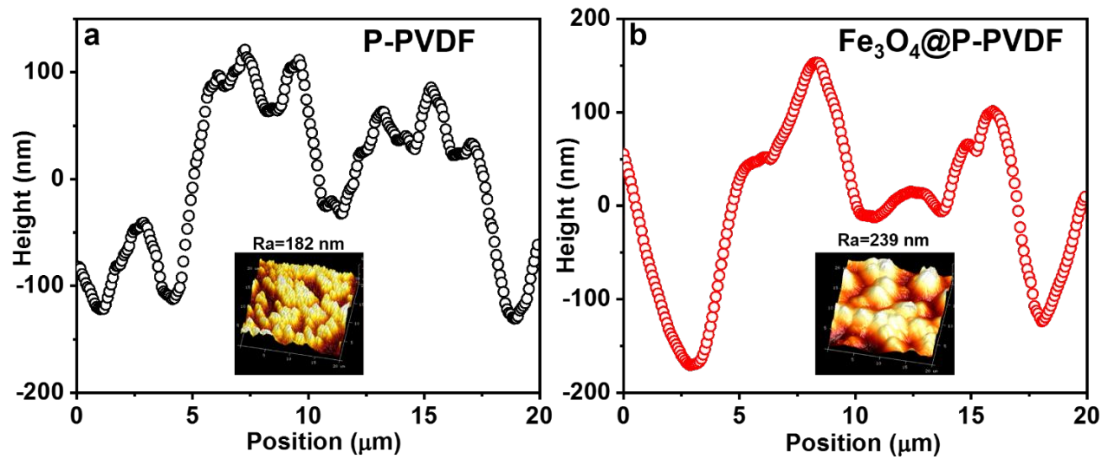
	Elemental mass fraction (%)					
	Fe	F	O	N	C	Si
Fe <sub>3</sub> O <sub>4</sub> @P-PVDF	0.83	12.79	18.09	5.91	58.41	3.96
P-PVDF	0.13	17.98	15.61	4.88	58.01	4.29



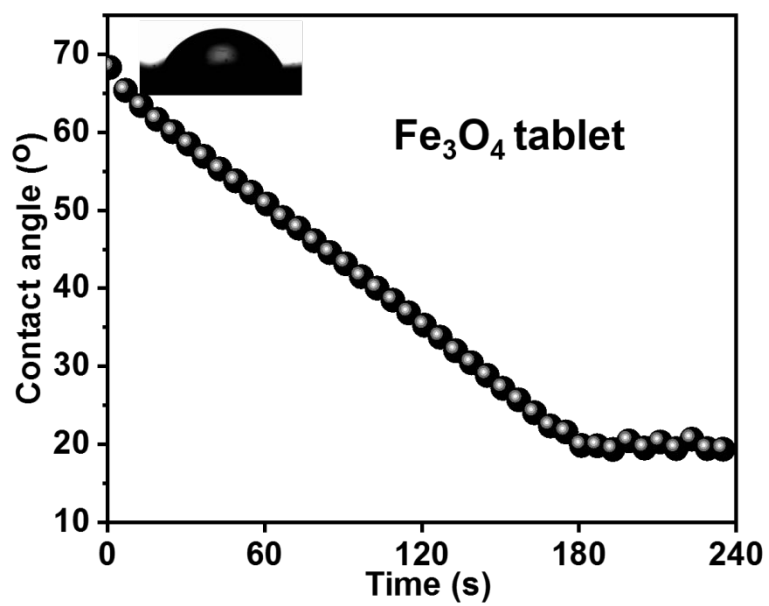
**Figure S1.** SEM images of (a, a1) surface and (b, b1) cross-section of the pristine PVDF membrane.



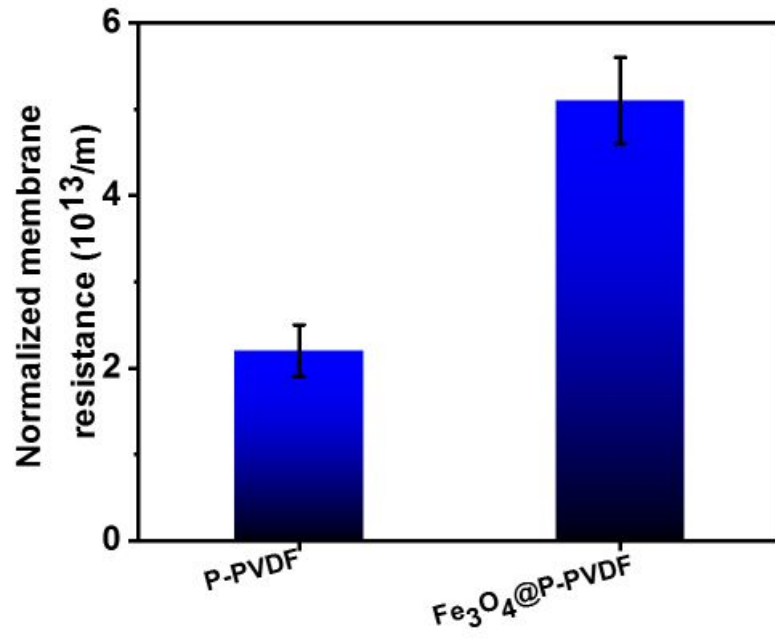
**Figure S2.** EDX image of Fe on the P-PVDF membrane top surface.



**Figure S3.** Scanning profiles of the membrane surfaces by AFM: (a) the P-PVDF membrane, (b) the  $\text{Fe}_3\text{O}_4@\text{P-PVDF}$  membrane. The inset pictures show the AFM phase images and roughness of the P-PVDF and  $\text{Fe}_3\text{O}_4@\text{P-PVDF}$  membrane surfaces.

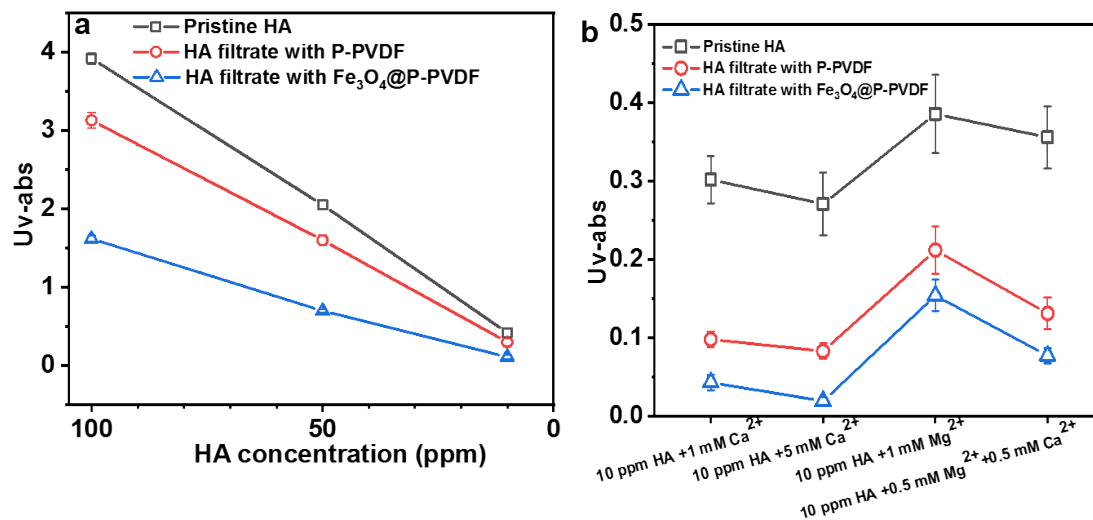


**Figure S4.** The dynamic water contact angle of  $\text{Fe}_3\text{O}_4$  tablet within 240 s.

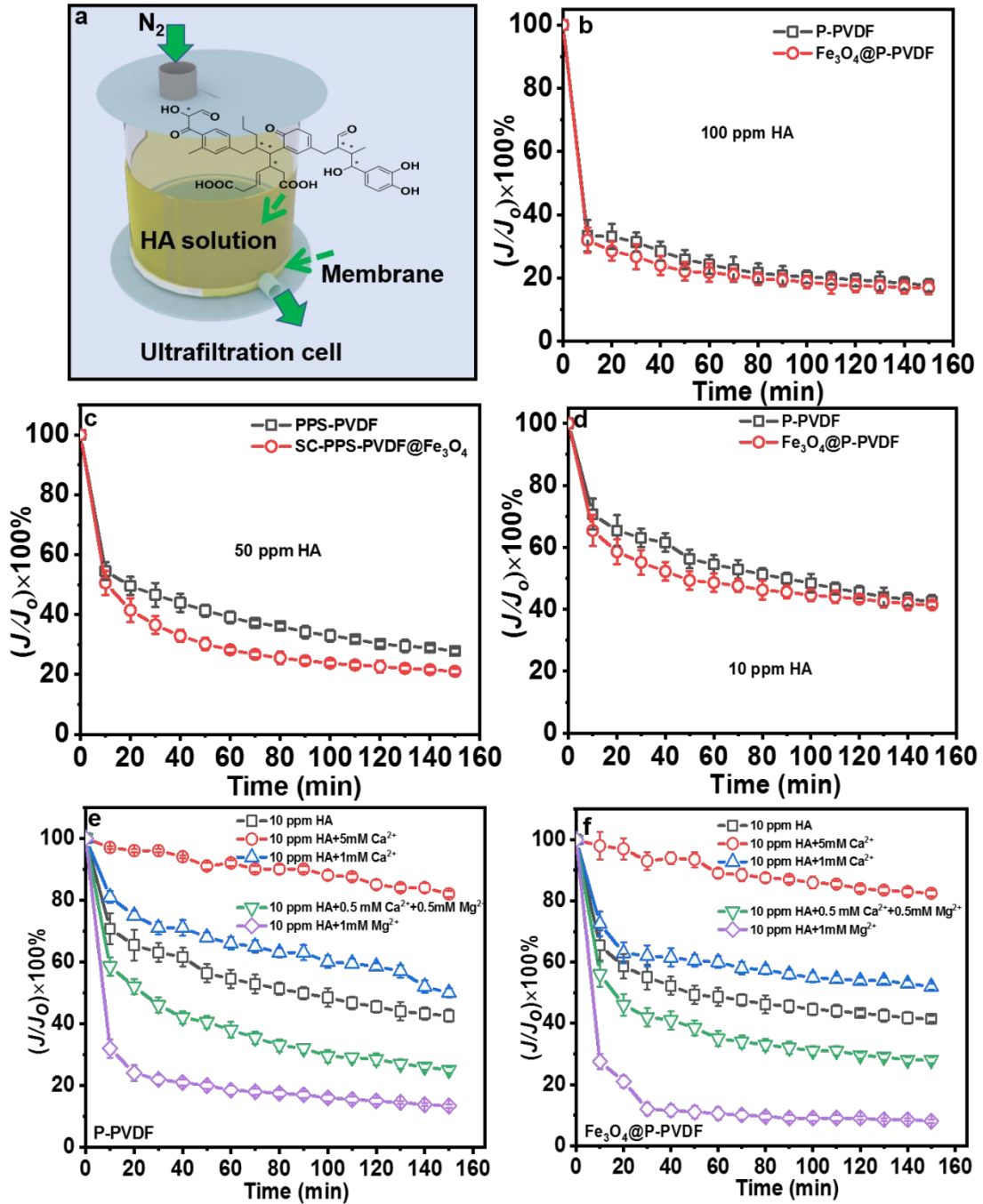


**Figure S5.** The hydraulic resistance of the P-PVDF and Fe<sub>3</sub>O<sub>4</sub>@P-PVDF membrane evaluated at 0.1 MPa.





**Figure S6.** (a) The UV absorbance of HA in the permeate through the membranes using HA solutions of different concentrations as the feed. (b) The UV absorbance of HA in the permeate through the membranes using 10 ppm HA solution containing Ca<sup>2+</sup> and/or Mg<sup>2+</sup> as the feed.



**Figure S7.** (a) The schematic of dead-end filtration with HA via an ultrafiltration cup. (b~d) the flux recoveries ( $J/J_0$ ) of P-PVDF and Fe<sub>3</sub>O<sub>4</sub>@P-PVDF membranes during the 150 min of continuous dead-end filtration with various HA concentration raw water (100 ppm, 50 ppm, and 10 ppm) under 0.1 PMa. The flux recoveries ( $J/J_0$ ) of (e) P-PVDF and (f) Fe<sub>3</sub>O<sub>4</sub>@P-PVDF membranes during the 150 min of continuous dead-end filtration with 10 ppm HA water solution containing various concentration Ca<sup>2+</sup> and Mg<sup>2+</sup> under 0.1 MPa.