

Supporting Information

One-Step Transformation of Highly Hydrophobic Membranes to Superhydrophilic and Underwater Superoleophobic Ones for High-Efficiency Separation of Oil-in-Water Emulsion

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Experimental Section

Materials. The poly(vinylidene fluoride) and poly(tetrafluoroethylene) microfiltration membranes (mean pore size 0.22 μm) were supplied by Membrane Solutions (USA). Polypropylene microfiltration membranes (PP, mean pore size 0.22 μm) were purchased from Membrane Gmbh (Germany). 3-aminopropyltriethoxysilane (APTES), Tannic acid (TA), tris(hydroxymethyl)aminomethane (Tris), and sodium dodecyl sulphate (SDS) were purchased from Aladdin (China). Ethanol, acetone, toluene and dichloroethane were provided by Tianjin Kermel Chemical Reagent Co., Ltd. (China). All the chemicals were used as received.

One-step superhydrophilic modification of various highly hydrophobic polymer membranes. Hydrophobic membrane (PVDF, PP, and PTFE membrane, copper mesh, stainless steel wire, and nylon mesh) was washed by ethanol for several times. Then the membrane pre-wetted by ethanol was stored in a Tris-HCl (pH=8.5)/ethanol solution (5/1, v/v) before use. Tannic acid (50 mg) was dissolved in Tris-HCl solution (20 mL, pH=8.5), and then ethanol (5 mL) dissolved with different amount of APTES (12, 24, 36, 48 and 60 mg) was added into the above tannic acid solution. A piece of pre-wetted membrane was immersed in the fresh mixture solution for 12 h at room temperature. Then the modified membranes were washed by deionized water thoroughly for at least 1 h to remove impurities from the membrane surface. In addition, for comparison, other membranes treated by sole TA or APTES were also prepared via immersion in HCl-Tris solution only containing TA or APTES, respectively. The detailed modification conditions have been listed in **Table S1**.

Table S1. The detailed modification conditions for PVDF, PP, PTFE membranes, and copper mesh, stainless steel wire, and nylon mesh.

Membranes	TA (mg mL ⁻¹)	APTES (mg mL ⁻¹)	Reaction Time (h)
PVDF-0	0	0	0
PVDF-1	2.0	0.5	12
PVDF-2	2.0	0.1	12
PVDF-3	2.0	1.4	12
PVDF-4	2.0	1.9	12
PVDF-5	2.0	2.4	12
PVDF-TA	2.0	0	12
PVDF-APTES	0.0	2.4	12
PP-0	0.0	0	0
PP-1	2.0	1.9	12
PTFE-0	0.0	0	0
PTFE-1	2.0	1.9	12
copper mesh	2.0	1.9	12
stainless steel wire	2.0	1.9	12
nylon mesh	2.0	1.9	12

Characterization. Surface morphologies and the element mapping of the pristine and modified membranes were characterized by scanning electron microscopy (SEM, S-4500, Hitachi, Japan) and energy-dispersive spectroscopy (EDX), respectively. The hierarchical structure and surface roughness of the pristine PVDF and PVDF-4 was characterized by Laser confocal microscope (OLS-4500, Olympus, Japan). Elemental analysis (EA) was carried out on a Vario MICRO CUBE elementar. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected on Spectrum One instrument (PerkinElmer, USA). Elemental composition of different membranes was performed by X-ray photoelectron spectroscopy (XPS, PerkinElmer, USA) with Al K α radiation (1486.6 eV) and the detection depth was less than 10 nm. Droplet or particle size distribution was detected by a dynamic light scattering (DLS)

measurement (ZetaPlus, Brookhaven Instruments, Holtsville, NY). The water contact angles, underwater oil contact angles, as well as the underwater oil roll-off angles were calculated by a contact angle measuring system (DSA100, Kruss GmbH, Germany). The contact angle values were calculated by averaging over more than six data at different position. In each process, 2 μL test liquid was dispensed at the membrane surface. The underwater anti-oil-adhesion properties of the modified membrane were evaluated by a preload-lift up process and a jet process, respectively. Pore sizes of the membranes were measured by an automatic pore size analyzer (3H-2000PB).

Emulsion separation experiments and stability test. 4 mL of oil was added into 120 mL of deionized water with 5 mg of SDS as emulsifier. The mixture was then stirred under 1000 rpm for 3 h. The droplet sizes are in the range of 1-20 μm under optical microscopy observation (BM-60XCC, China). Note that, there are also abundant nano-sized oil droplets (about 500 nm) in the emulsion according to the data from dynamic light scattering (Please see **Figure S 19**).

The pure water flux and oil-in-water emulsion separation performances of MF membranes were carried out by a vacuum driven filtration system (F1040LA, Beijing Synthware Glass Co. Ltd.) at 0.08 MPa (vacuum degree-0.08 MPa). The oil content in the filtrates was extracted by CCl_4 and tested by infrared spectrometer oil content analyser (OIL 480). The water flux and oil rejection of the membrane were obtained by the following equations, respectively:

$$Flux = \frac{V}{At} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \quad (2)$$

where V is the permeate volume (L), A is the effective membrane area (m²), and t is the permeation time (h). R is the oil rejection rate, and C_p and C_0 are concentrations of oil in the collected water after filtration and the pristine emulsion. The active area of membrane is 12.56 cm².

The stability of the modified membrane was evaluated by investigating the changes of contact angles and emulsion separation performance after repeatedly rinsing treatment (3000 r/min). Ten cycles were carried out, and each cycle lasts for 3 h.

Moreover, the stability of the modified membrane (PVDF-4) in acid (pH=1, 3, and 5), alkali (pH=9 and 12) and salt (saturated sodium chloride) solutions has been also investigated, respectively. The PVDF-4 was immersed into the above mentioned solution for at least 12 h, and the treated PVDF-4 was washed by DI water and dried under 40 °C for further characterization. The water contact angles, underwater oil contact angles, and SEM images of the PVDF-4 after stability test are investigated to evaluate the stability of the PVDF-4.

Results and Discussion

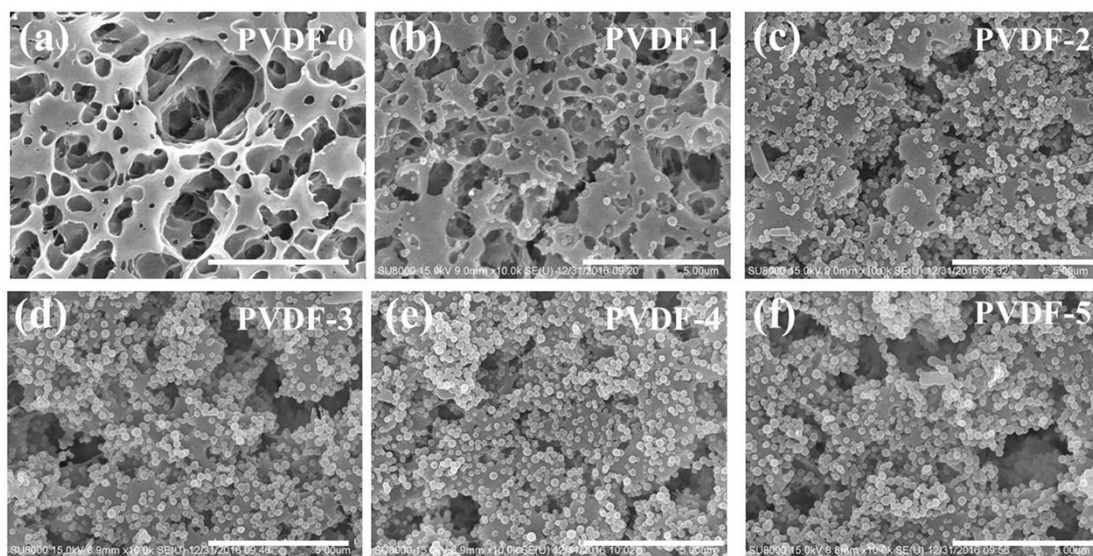


Figure S1. SEM images (low magnification) of the (a) PVDF-0, (b) PVDF-1, (c) PVDF-2, (d) PVDF-3, (e) PVDF-4, and (f) PVDF-5. The scale bar is 5 μm .

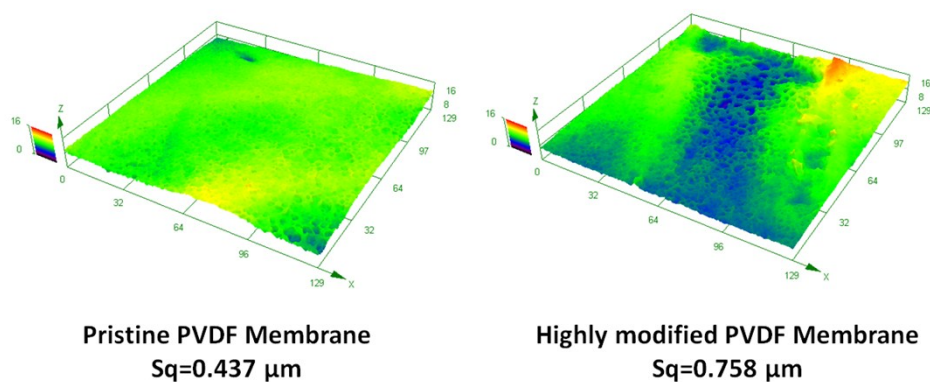


Figure S2. Laser scanning confocal microscopy (LSCM) images of the pristine PVDF membrane (PVDF-0) and the highly modified PVDF membrane (PVDF-4).

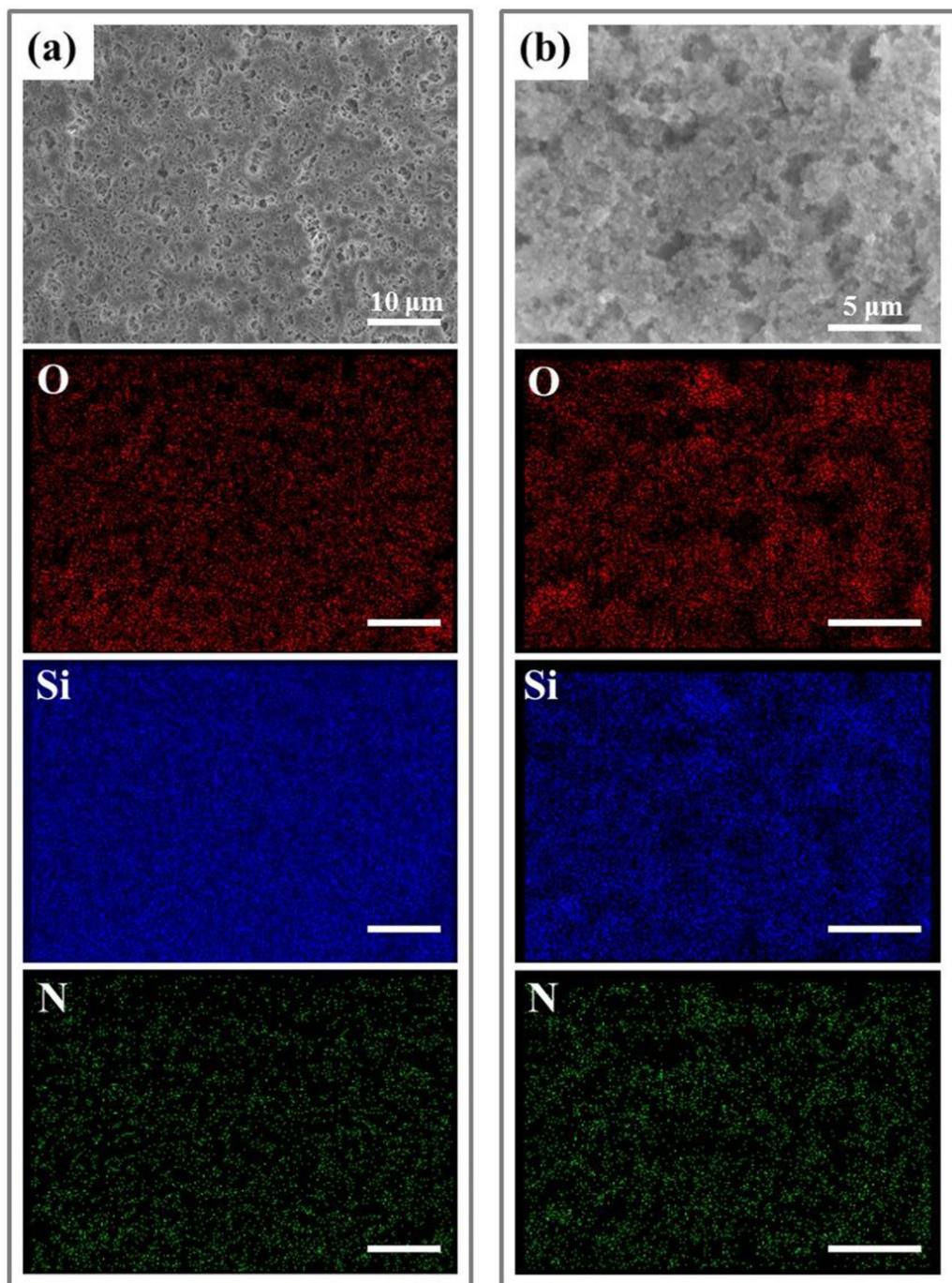


Figure S3. SEM images and EDX mappings of the (a) PVDF-1 and (b) PVDF-4.

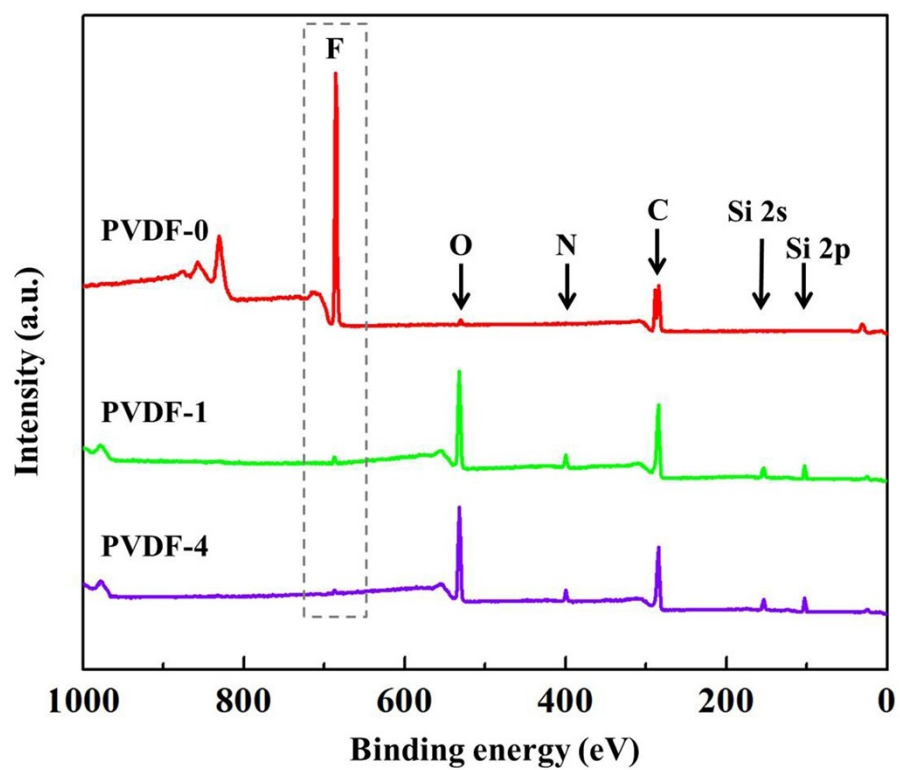


Figure S4. XPS spectra of the PVDF-0, PVDF-1 and PVDF-4.

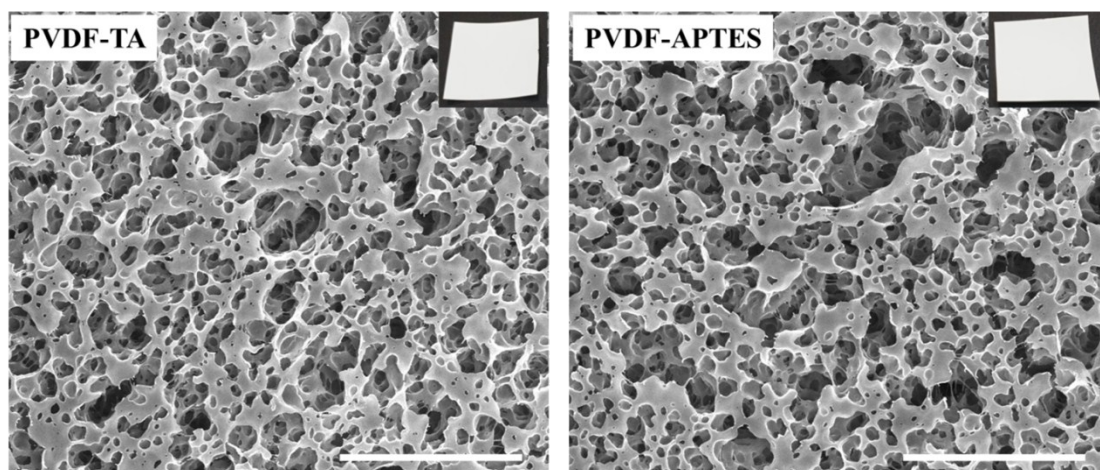


Figure S5. SEM images of the PVDF-TA and PVDF-APTES. The insets are the corresponding photographs. The scale bar is 10 μm .

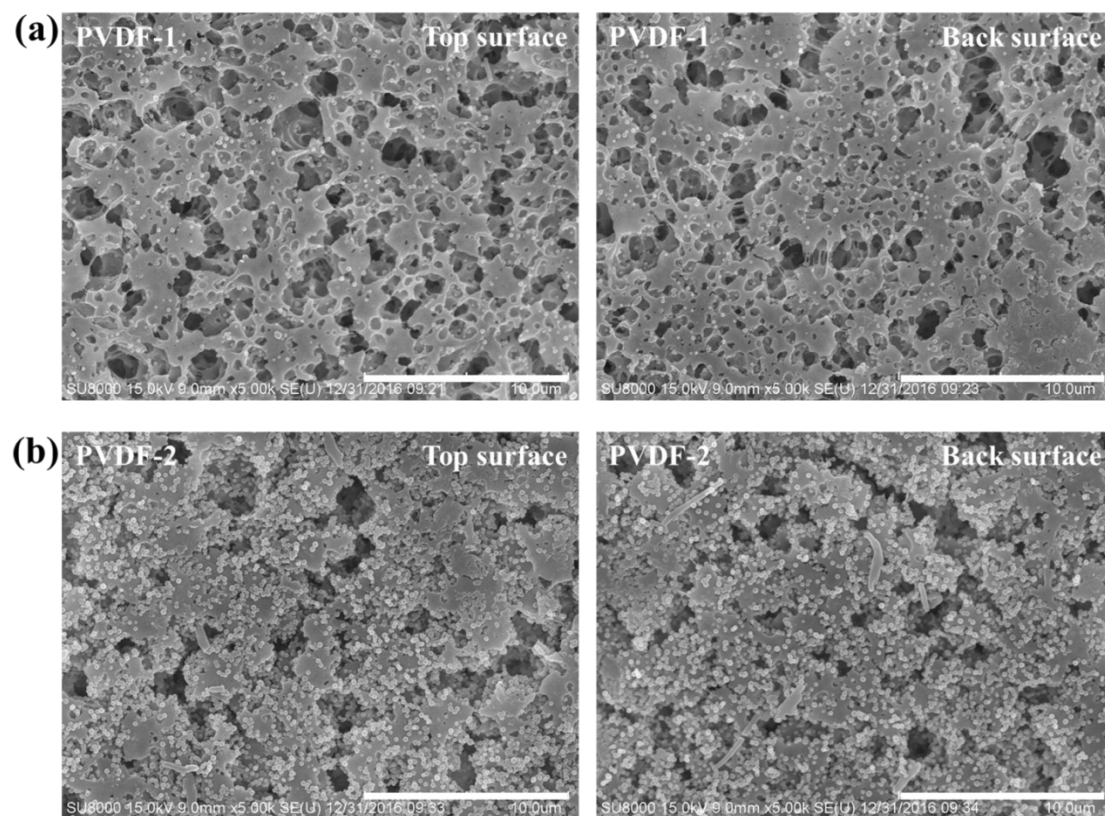


Figure S6. SEM images (low magnification) of the top and back surfaces of (a) PVDF-1 and (b) PVDF-2. The scale bar is 10 μm .

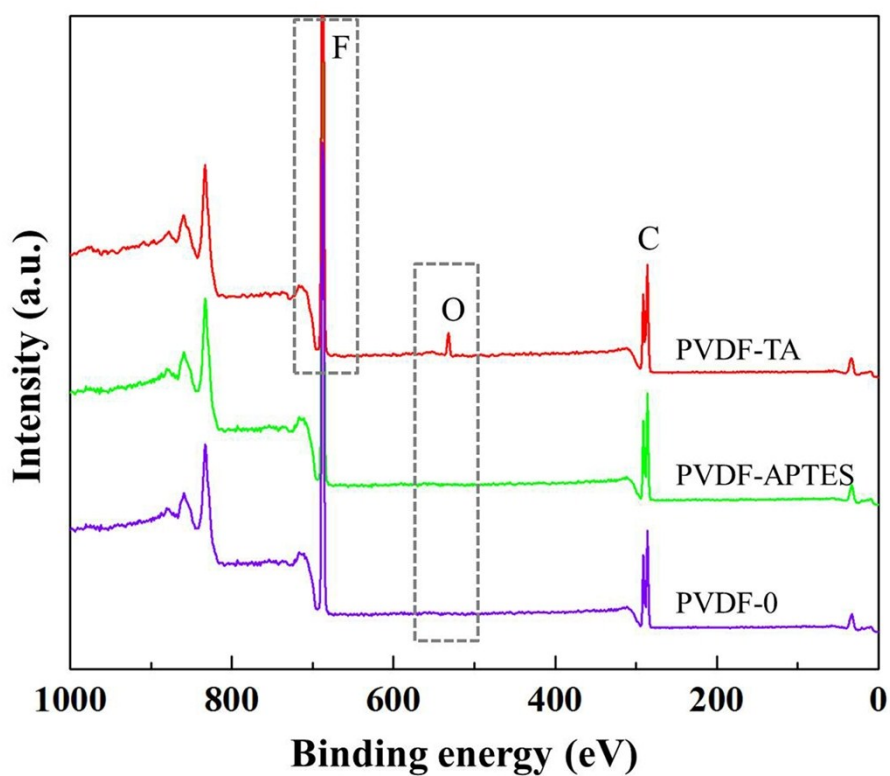


Figure S7. XPS spectra of the PVDF-0, PVDF-APTES and PVDF-TA.

As shown in Figure S7, there is almost no difference for the XPS spectra of the PVDF and the PVDF-APTES, while O element was detected on the PVDF-TA surface. These results demonstrate that sole APTES cannot modify the hydrophobic PVDF membrane, while TA alone can. Note that the F element can also be detected on the PVDF-TA surface, indicating the TA-based coating should be thin enough.

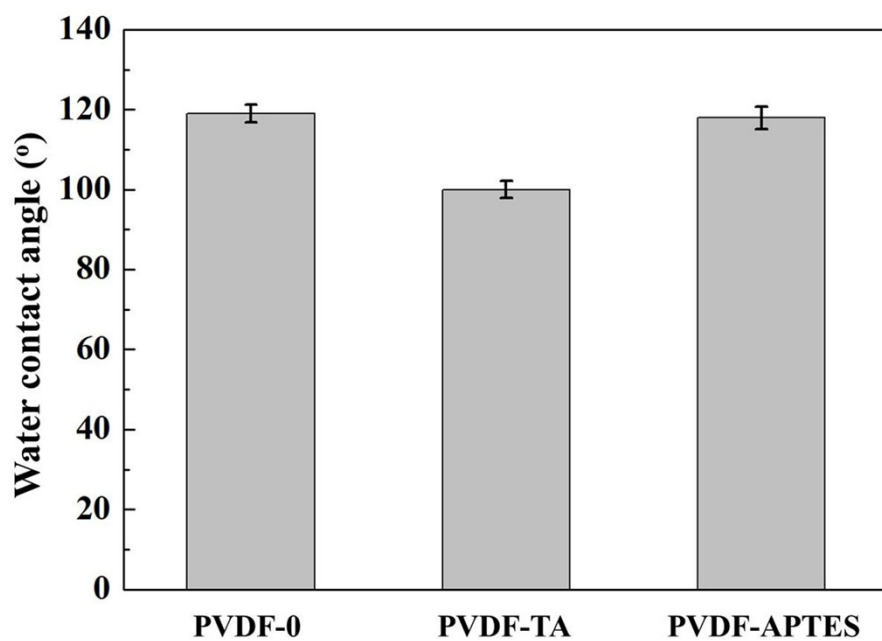


Figure S8. Water contact angles of the PVDF-0, PVDF-TA and PVDF-APTES.

As shown in **Figure S8**, there is almost no difference for the water CA of PVDF-0 and PVDF-APTES, which can further indicate sole APTES cannot realize the modification of hydrophobic PVDF membrane. Differently, the PVDF-TA exhibits lower water CA (about 100°), implying the formation of TA-based coating on membrane surface.

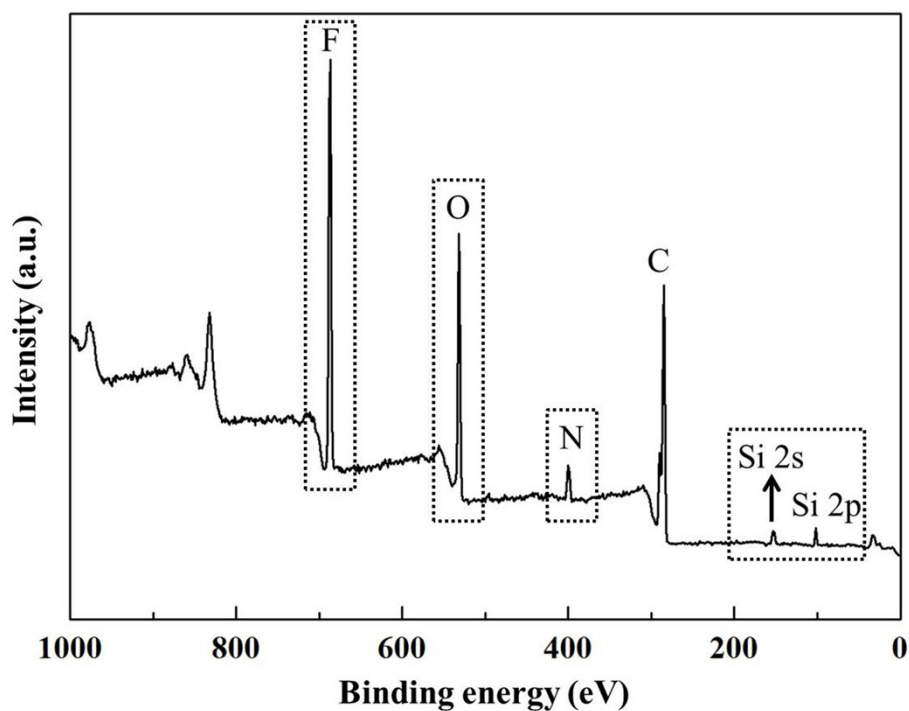


Figure S9. XPS spectrum of the PVDF membrane treated by the TA and APTES mixture for 40 min.

Besides the O elements, new elements such as N and Si are detected on the modified membrane, indicating the formation of hybrid coating on membrane surface. The N and Si elements on membrane surface are derived from the hydrolysis product of APTES. As has been proved, sole APTES cannot realize the modification of PVDF membrane, thus the introduction of N and Si should be ascribed to the reaction between the hydrolysis product of APTES and the formed TA-based coating. In

addition, the peak of F element is still strong, implying the formed hybrid coating in this period is thin enough.

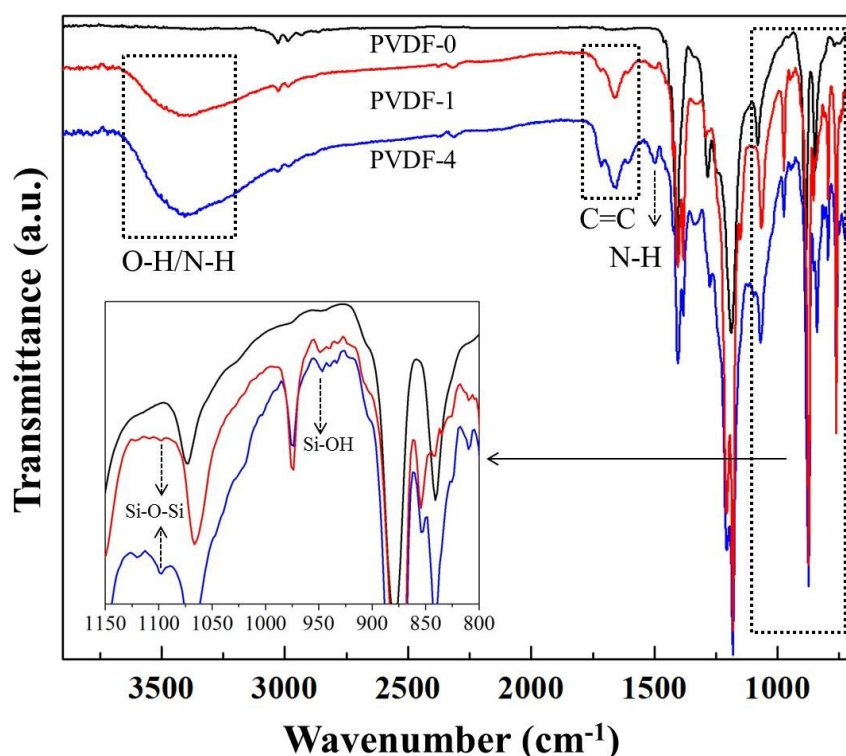


Figure S10. ATR-FTIR spectra of the PVDF-0, PVDF-1 and PVDF-4.

After modification, several new absorption signals appear. The peaks between 1600-1450 cm^{-1} are derived from the benzene skeleton C=C stretch vibration band, which is the characteristic adsorption of benzene. The peaks at 1097 and 947 cm^{-1} are due to the antisymmetric stretching vibration of Si-O-Si and symmetric stretching vibration of Si-OH. These results indicate that both TA and APTES are participated in the construction of these distinct coatings on the modified membranes. Note that N-H

bending vibrations (1506 cm^{-1}) were observed on the modified membranes. Besides, the C-H out-of-plane bending vibration band (867 cm^{-1}) of 1,2,3,5-tetrasubstituted benzene gradually decrease, while the C-H out-of-plane bending vibrations band ($838\text{--}819\text{ cm}^{-1}$) of pentasubstituted benzene gradually enhance from the PVDF-1 to PVDF-4. These results suggest that Michael addition and Schiff base reaction occur during the modification process. The broad absorbance between 3600 and 3100 cm^{-1} should be ascribed to O-H/N-H stretching vibrations. These hydroxyl groups should be derived from the unoxidized phenolic hydroxyl groups of TA and the rearrangement of benzene after Michael addition and Schiff base reactions. Besides, the hydrolysis of APTES also introduces some hydrophilic hydroxyl groups on the modified membranes. These hydrophilic groups, as well as the formed hierarchical structures on the modified membranes, may significantly improve the hydrophilicity of the modified PVDF membrane.

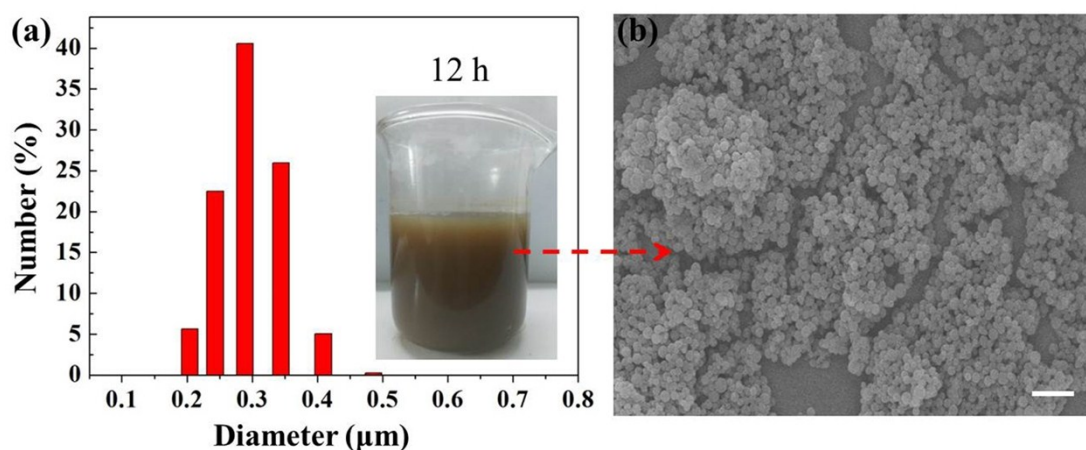


Figure S11. (a) Size distribution of the formed nanoparticles in the TA-APTES mixture solution for preparation of PVDF-4 at 12 h. The insets are the corresponding

photo-pictures of the mixture solution. (b) SEM image of the nanoparticles formed in the mixture solution in a. The scale bar is 1 μm .

Table S2. The detailed chemical composition of the colloidal nanospheres.

Composition (At. %)			
C	N	O	Si
49.1%	6.7%	37.6%	6.6%

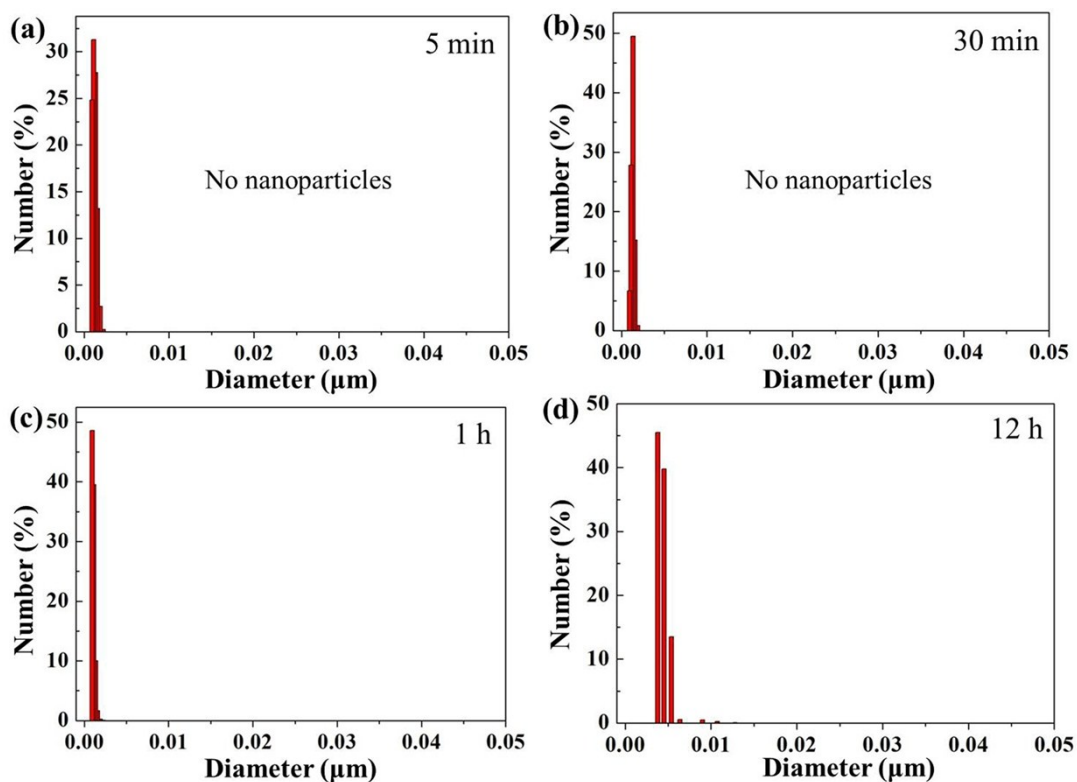


Figure S12. Size distribution of the sole APTES without TA in mixture solution.

For comparison, we also prepared mixture solution that without TA. No solid nanoparticles can be obtained from the mixture solution even after 12 h. As shown in **Figure S12**, the size distribution from 1-2 nm should be due to a small quantity of

solubilized APTES in the mixture. Thus those solid nanoparticles (200~400 nm) decorated on membrane surface are not the hydrolysis product of APTES.

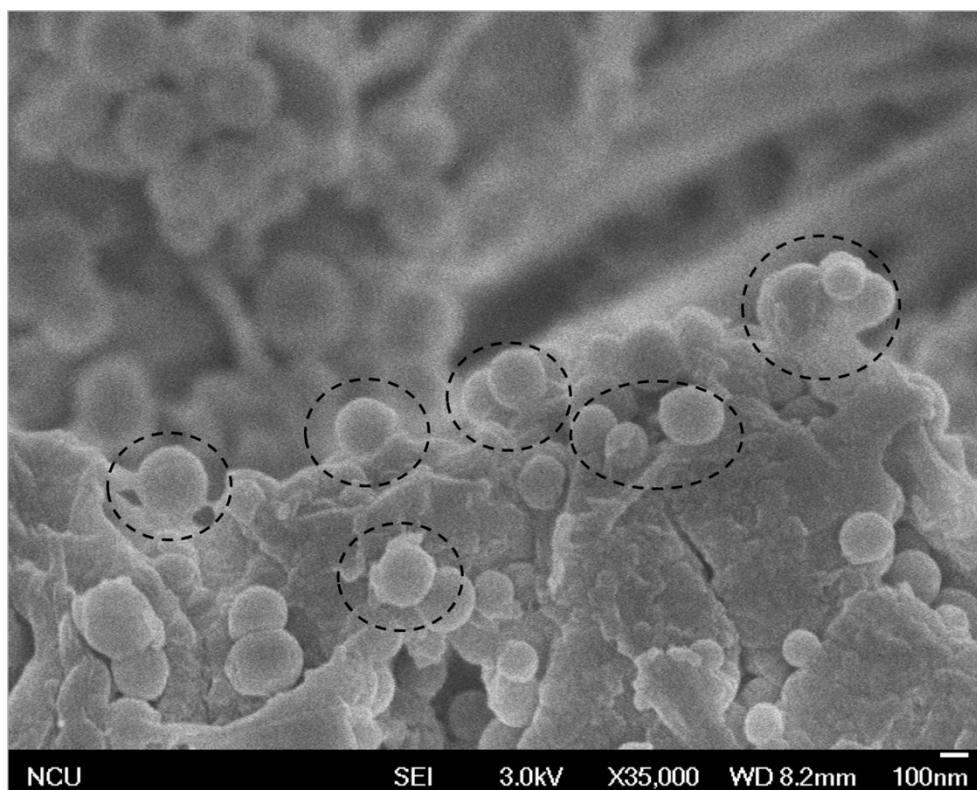


Figure S13. SEM image of the PVDF-4 (oblique view).

Note that, the fortified coating like binder is formed around the contact site between nanospheres and the surface layer (see the area in the dotted circle), which can endow the nanospheres with desirable stability on the membrane surface.

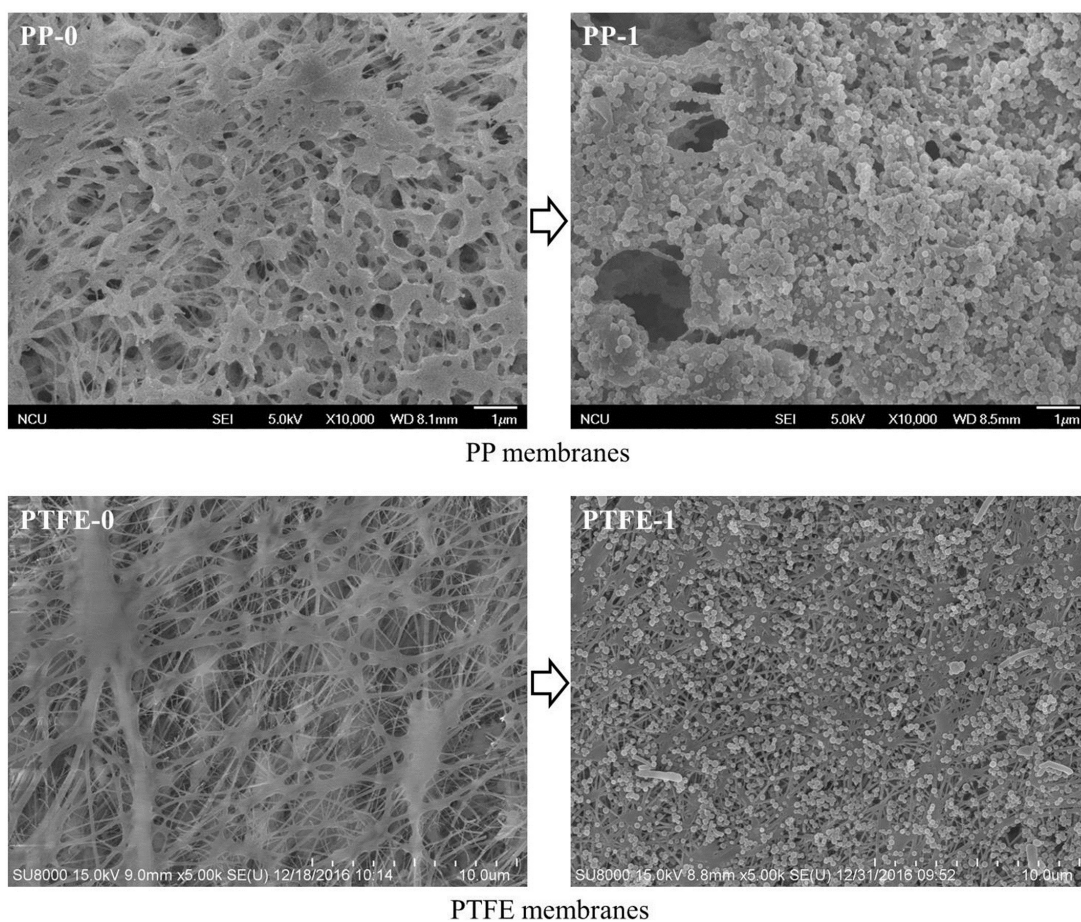


Figure S14. SEM images (low magnification) of the PP-0, PP-1, PTFE-0 and PTFE-1.

The PP-0 and PTFE-0 are the pristine membrane, while the PP-1 and PTFE-1 are the membranes modified by both TA and APTES. Nanospheres similar to that on PVDF-4 are observed on both PP-1 and PTFE-1.

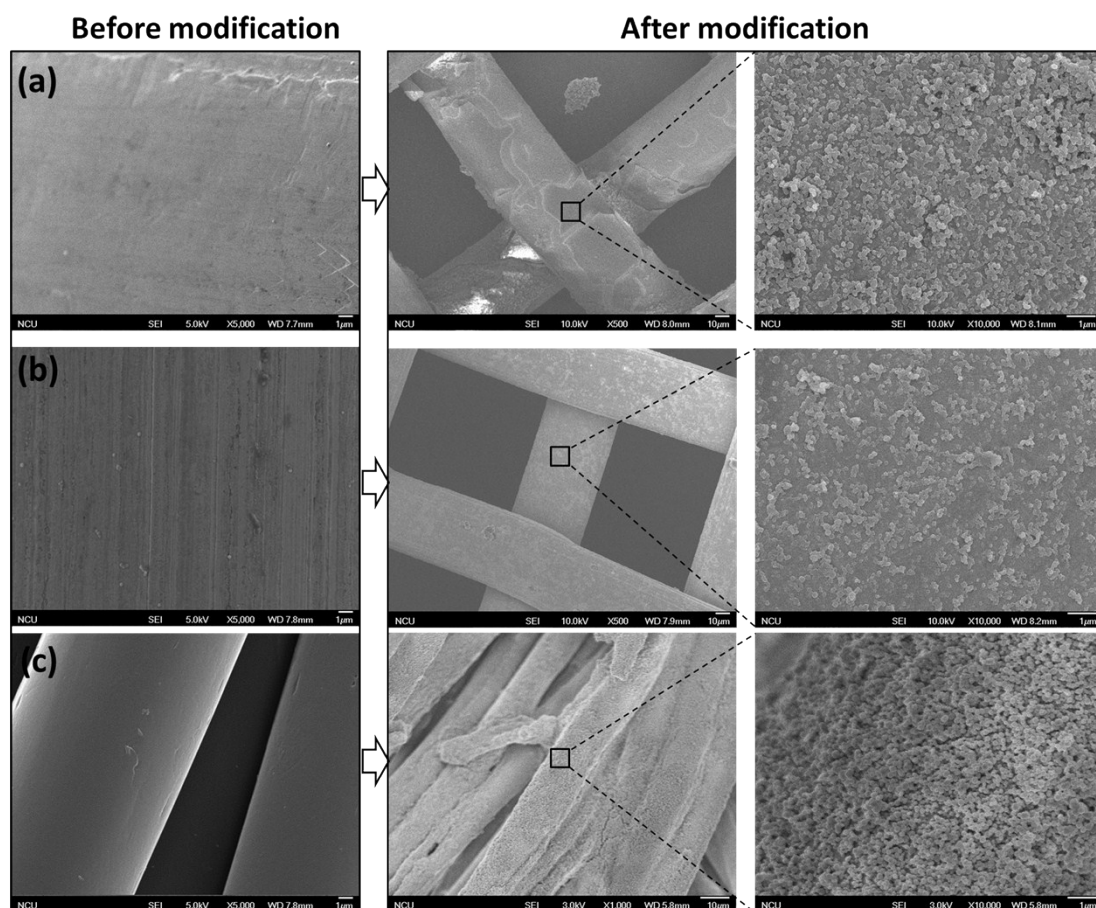


Figure S15. SEM images of the (a) copper mesh, (b) stainless steel wire and (c) nylon mesh before and after modification via the one-step strategy based on TA and APTES.

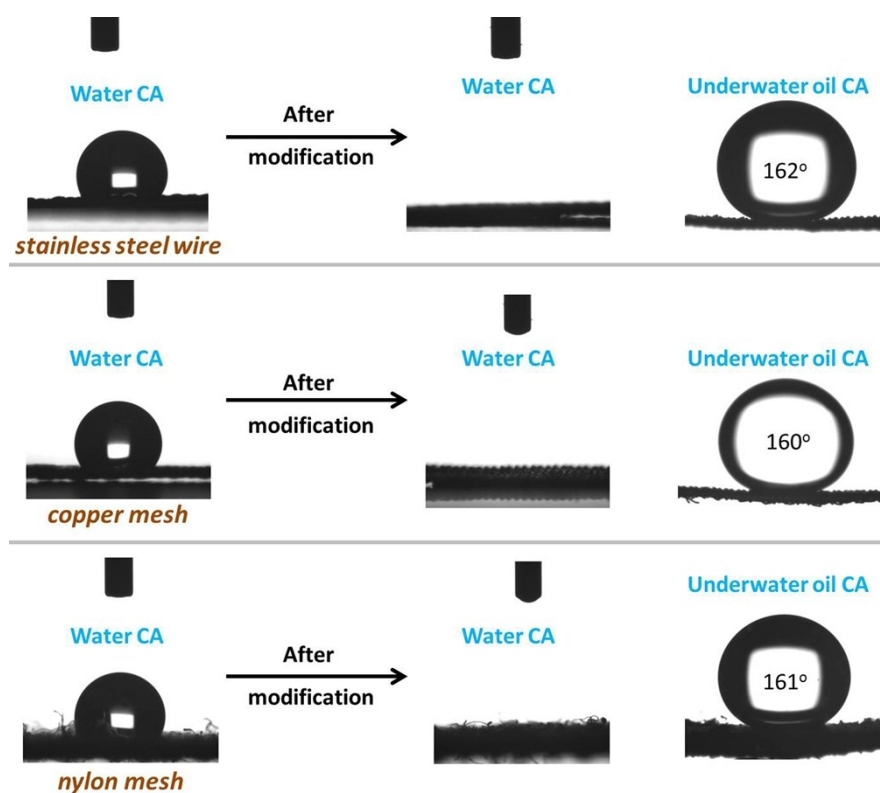


Figure S16. The water CA of different pristine substrates (copper mesh, stainless steel wire and nylon mesh), and the water CA and underwater oil CA of the modified substrates obtained via the one-step strategy based on TA and APTES.

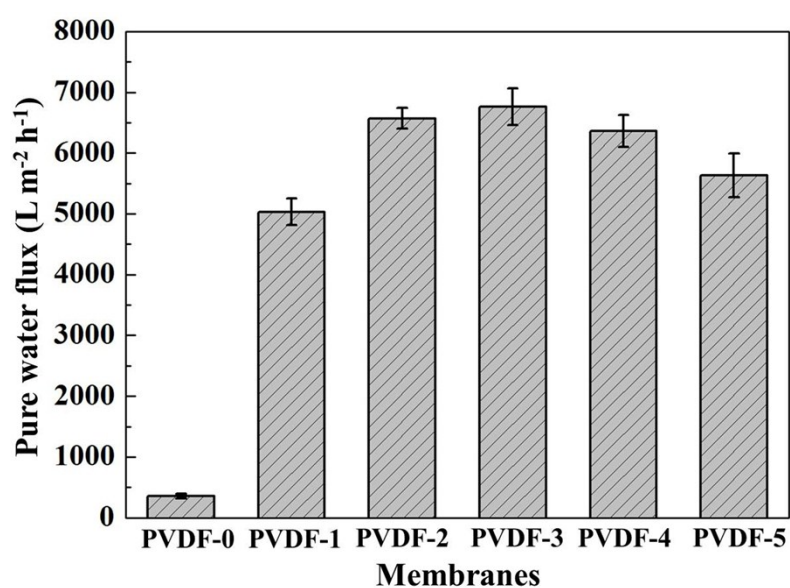


Figure S17. Pure water flux of pristine and modified PVDF membranes.

The water flux is one of the important properties of filter membranes. Under the same operation pressure, the water flux is related to the pore size and the hydrophilicity of the membranes.^{1, 2} The stronger the hydrophilicity, the higher the water flux. And the larger the pore size, the higher the water flux. As shown in **Figure S17**, the water flux of the pristine membrane is only 358 L m⁻² h⁻¹ due to the strong hydrophobicity. With the increase of the hydrophilicity, the water flux keeps rising from PVDF-1 to PVDF-3, and reaches the maximum value (6762 L m⁻² h⁻¹), which is about 18.9 times that of pristine membrane. For the superhydrophilic PVDF-4 and PVDF-5, although a little decrease of the water flux is observed, the water flux of PVDF-4 and PVDF-5 is still 17.8 and 15.7 times that of the pristine membrane, respectively. The decrease of the water flux can be explained by the decreased pore size caused by the dense nanohierarchical structures on the membranes.

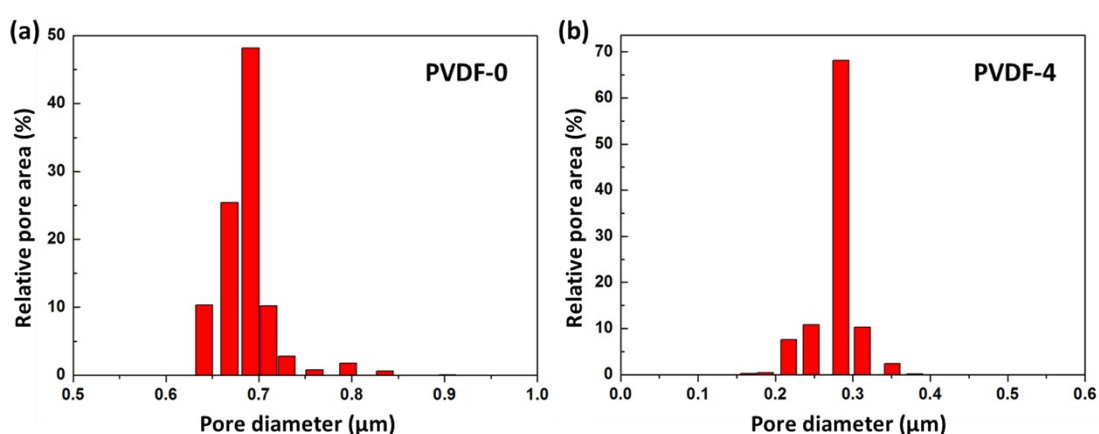


Figure S18 The pore size distribution of the pristine PVDF membrane (PVDF-0) and the modified membrane (PVDF-4).

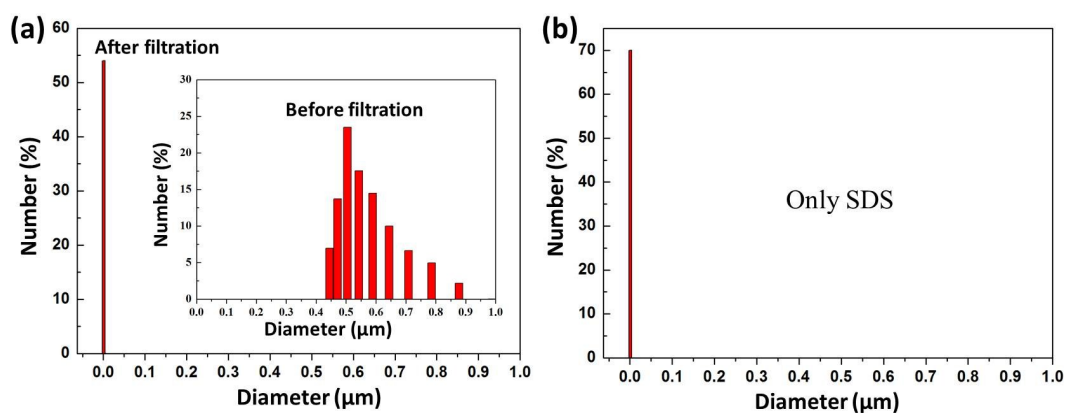


Figure S19 (a) The DLS data of the obtained filtrate after filtration. The inset is the DLS data of the pristine emulsion before filtration. (b) The DLS data of a water solution that only contains SDS.

Before filtration, there are abundant nano-sized oil droplets in the emulsion. After filtration by the PVDF-4, the nano-sized droplets disappeared, indicating the small oil droplets have been removed by the PVDF-4. Note that, the new sharp peak appears at 1 nm is due to the residual surfactants in the filtrate rather than residual oil droplets.^{3, 4} A similar peak around 1 nm is also observed in the SDS solution (sole SDS dissolved in water), confirming the sharp peak is caused by residual SDS in the filtrate.

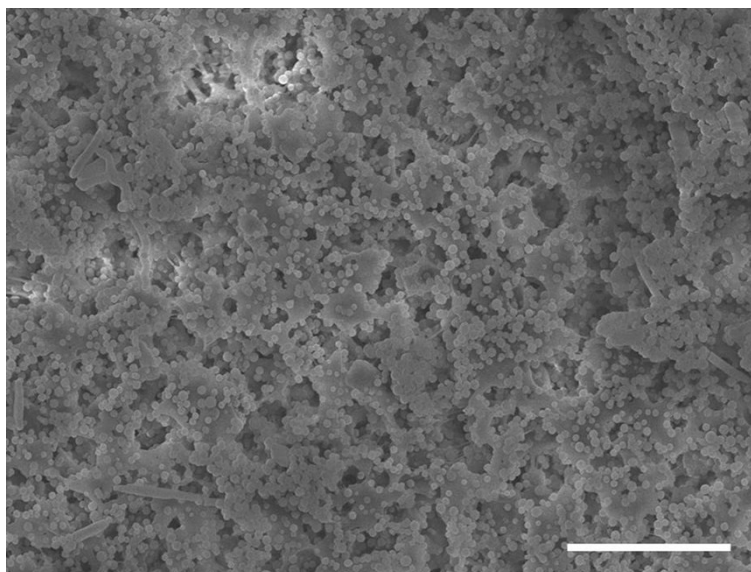


Figure S20. The SEM image of the PVDF-4 after 10 cycles rinsing-filtration process. The scale bar is 5 μm .

Solutions Contact angles (CA)	After treated by different solutions for 12h					
	pH=1	pH=3	pH=5	pH=9	pH=12	Saturated sodium chloride
Water CA						
Underwater Oil CA						

Figure S21. The water CA and underwater oil CA of the PVDF-4 after treated by acid, alkali and salt solutions for 12 h, respectively. The oil used for test is dichloroethane.

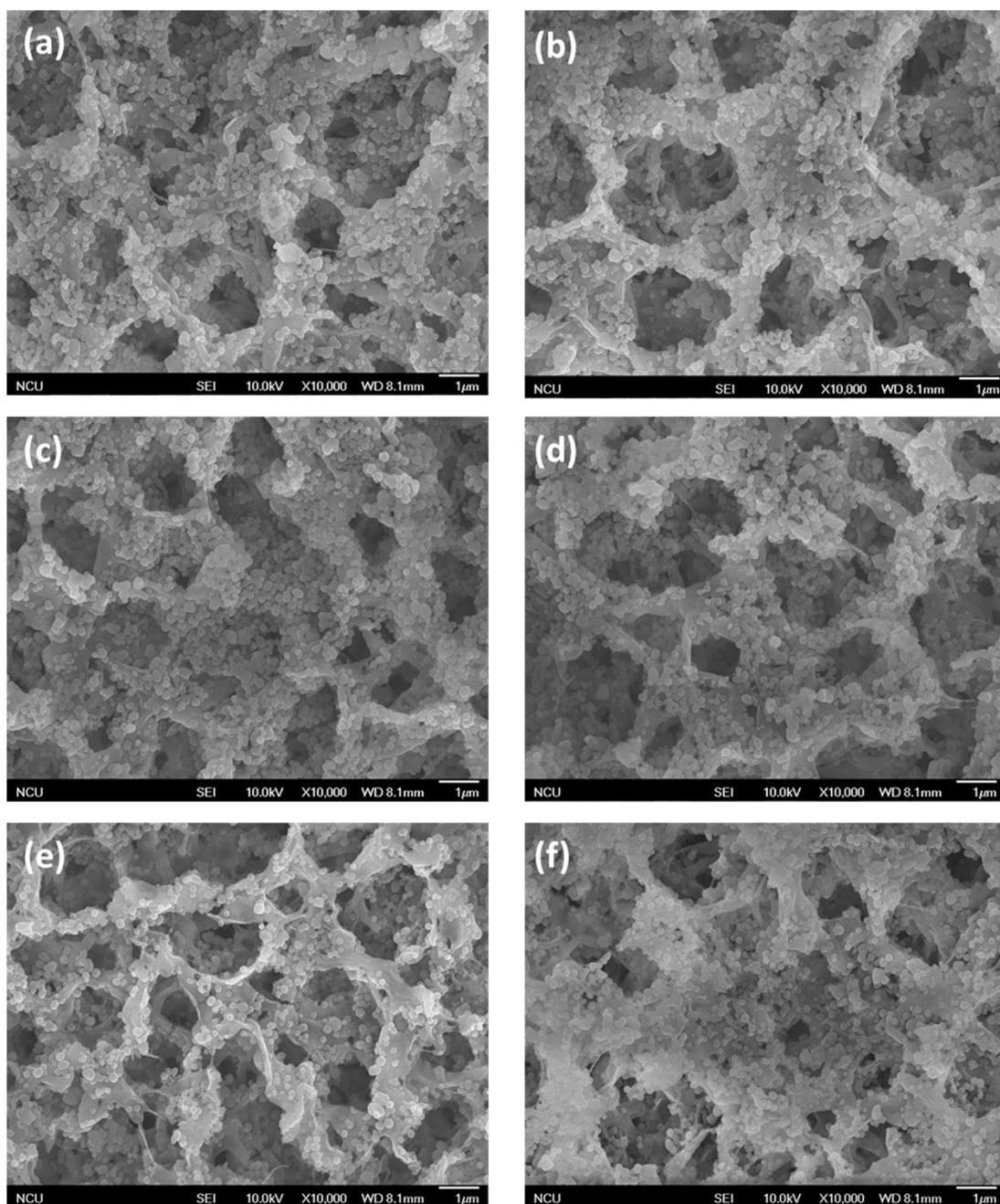


Figure S22. SEM images of the PVDF-4 after being treated by (a) acid (pH=1), (b) acid (pH=3), (c) acid (pH=5), (d) alkali (pH=9), (e) alkali (pH=12) solutions and (f) salt solution (saturated sodium chloride) for 12 h, respectively.

References

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