Supporting Information

Superoleophobic micro-nanostructure surface formation of PVDF membranes by tannin and condensed silane coupling agent

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Abstract: A tannin-based hybrid coating was coated on the PVDF membrane surface through a simple one step co-deposition of tannin and KH550. A micro/nano hierarchical structure was formed on the PVDF membrane surface through hydrolysis/condensation of KH550 and Michael addition reaction between oxidized tannin and amino revealed by the field-emission scanning electron microscopy, atomic force microscopy and fourier transform infrared spectroscopy, which established a harsh surface. Abundant hydrophilic groups and high surface roughness endowed modified membranes with high hydrophilicity and underwater superoleophobicity. The modified PVDF membranes possess excellent oil/water separation and antifouling performance due to the underwater superoleophobicity. Moreover, the modified membrane exhibited outstanding stability.

Materials.

Commercial PVDF microfiltration membranes were purchased from Membrane Solutions (Chain). Tara powder, which is made in Peru, was bought from the Shanghai CelChem Company. (3-aminopropyl) triethoxy-silan (KH550) was obtained from Jianghan Fine Chemical Co., Ltd. Tween-80, sodium hydroxide, tris (hydroxymethyl)-aminomethane (Tris) and all organic solvents were purchased from the Sinopharm Chemical Reagent Co., Ltd (China). All chemicals were used as received. Deionized water was obtained from a deionized water generator system (RS-10B, XINRUI, Chain).

Characterizations

Morphology and chemical composition: The membrane surface morphology and micro-nonastructure were observed by a field-emission scanning electron microscope (FESEM, S4800, Hitachi, Japan) with an accelerating voltage of 5.0kV, and all samples were sputtered with gold before measurement. An atomic force microscopy (AFM, Dimension FastScan, Bruker, Germany) with ScanAsyst model was measured to further study the roughness of membranes surface. The chemical composition of the modified and unmodified membranes was analyzed via X-ray photoelectron spectroscopy (XPS, Escalab-250Xi, ThermoFisher, Britain) with Al-Ka as the radiation source. The functional groups on the membrane surface were determined via attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, ThermoFisher, USA).

Contact angle: The water contact angle (WCA) and underwater oil contact angle (OCA) of the membrane surface were measured using a contact angle test system (JC2000C, Zhongchen, China), and at least five measurements were taken at different positions on each sample.

Deposition ratio: The deposition ratio of the modified membranes was calculated using **Equation S1**, which employs a simple weighing method:

$$DR = \frac{W_x - W_0}{W_o} \times 100\%$$

Equation S1

Where *DR* refers to the deposition ratio, W_x and W_0 are the weight of the modified membranes, respectively.

Filtration performance: The filtration performance was measured on a vacuum driven filtration system at a stable pressure (-0.09MPa) as shown in Figure S4. The toluene-in-water emulsion was prepared by mixing toluene and water (1:99, v/v) with the addition of 0.02 mg Tween-80 per milliliter of emulsion under a high stirring speed for 5h. Pure water and emulsion filtration flux values were calculated by **Equation S2** and **Equation S3**.

$$J = \frac{V}{A\Delta t}$$

Equation S2

$$FRR = \frac{J_{w1}}{J_{w2}} \times 100\%$$

Equation S3

J was the flux value (L/m^{2}h) including pure water flux (J_w) and oil/water emulsion filtration flux (J_e). *V, A, Δt* represented the volume of permeated liquid, membrane area and permeation time

respectively. J_{w1} and J_{w2} refer to the pure water flux before and after oil/water emulsion filtration respectively.

Results and Discussion

Figure S1 is the images of the pristine and modified PVDF membranes. Compared with the PDA modified membranes in other reports, the tannin-based coating layer just have slight changed in color, which indicates that the tannin-based coating will have more widely application such as modification of optical thin film.

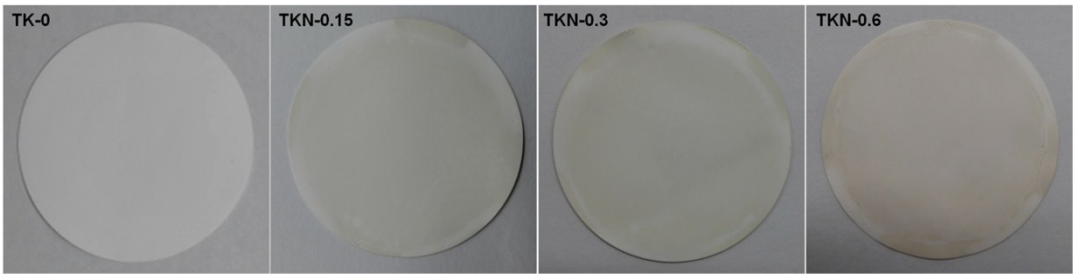

Figure S1. *Images of the pristine and modified PVDF membranes*

Figure S2 shows the deposition ratio of the modified PVDF membranes. It can be seen that as the increase of the content of KH550, the DR of the modified membranes are increasing linearly. It indicates that more hybrid coating are anchored on the membrane surface which can be explained that more and bigger micro/nano particles will form and bond on the membrane surface as the increase of the content of KH550 co-deposited with tannin.

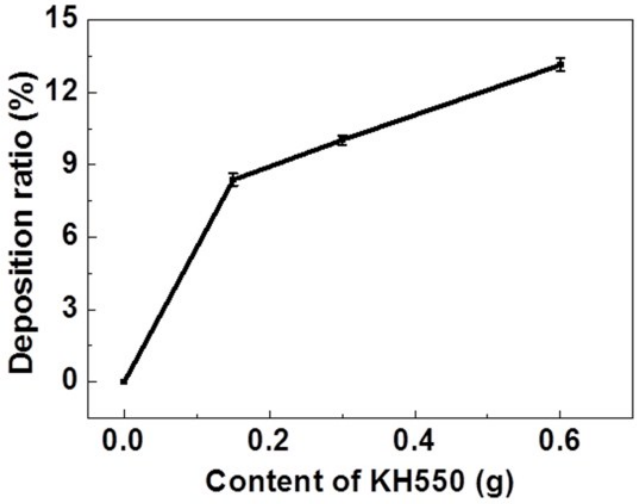

Figure S2. *Deposition ratio of the modified PVDF membranes*

Figure S3 is ATR-FTIR spectra of the pristine and modified PVDF membranes. Four notably absorption peaks at 1608cm^{-1}, 1499cm^{-1}, 1323cm^{-1},and 1098cm^{-1} were detected, which assigned to skeletal vibration of aromatic rings, N-H bending vibrations, C-N stretching vibration and Si-O-Si

stretching vibration respectively. These imply that a lot of hydrophilic groups have coated on the hydrophobic PVDF membrane surface, which can significantly improve its hydrophilicity.

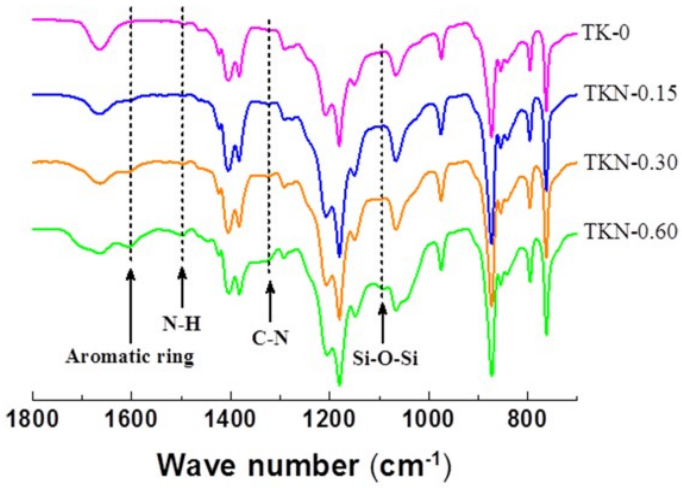

Figure S3. *ATR-FTIR spectra of the pristine and modified PVDF membranes*

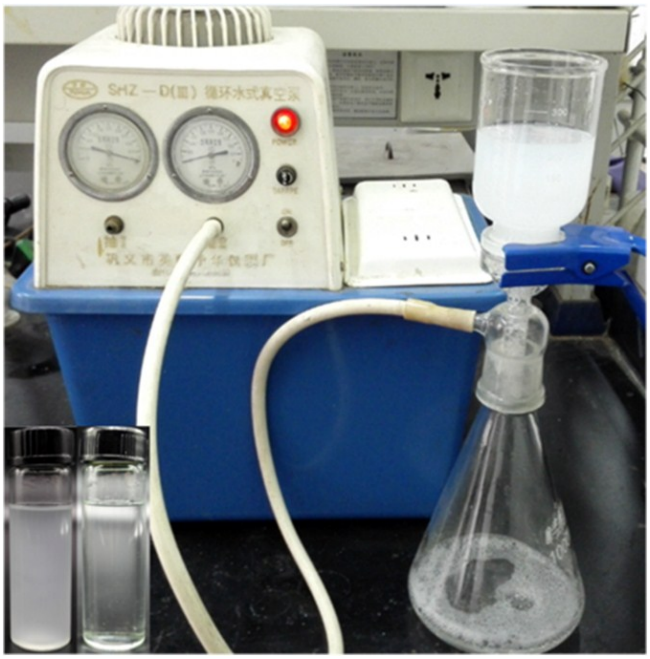

Figure S4. *The picture of emulsion separation process, insert image is the emulsion before (left) an after (right) filtration.*

Table S1. *Elemental composition of various PVDF membranes detected by XPS*

Membrane	Composition (at %)					Atomic ratio		
	F	C	O	N	Si	Si/O	Si/C	O/C
TK-0	49.12	47.75	1.75	1.38	/	/	/	0.037
TKN-0.15	15.93	63.77	16.54	3.31	0.46	0.028	0.007	0.259
TKN-0.3	15	61.73	18.84	3.27	1.16	0.062	0.019	0.305
TKN-0.6	13.64	61.93	19.24	3.65	1.54	0.08	0.025	0.311