Supplementary Information

Optimized preparation conditions of TiO₂ deposited on SiO₂ solid

superacid nanotubes as filler materials

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S1. Hammett acidity H₀ test.

The solid acidity H_0 of TSANs was determined by Hammett indicator method. When the adsorption of indicator on the surface of a solid acid is balanced, the reaction between its surface acid sites and indicator accords with the following relation:

$$H_0 = pKa - Lg \frac{[AB]}{[B]} \tag{1}$$

Where Ka is the ionization constants of indicator, [B] is concentration of indicator (g/L), [AB] is the concentration of indicator conjugate acid (g/L).

1) Standard curve of anthraquinone/ethanol solution

Anthraquinone/ethanol solutions with anthraquinone concentration of 0.01 g/L, 0.02 g/L, 0.05 g/L, 0.08 mg/L and 0.1 g/L were prepared, respectively. With ethanol as reference fluid, the corresponding absorbance value was tested by UV spectrophotometer under 360 nm wavelength. Standard curve was obtained by linear regression of data. Fig. S1 is standard curve of anthraquinone/ethanol solution.



Fig. S1. Standard curve of anthraquinone/ethanol solution

The equation of standard curve is

$$Y = 1.3072[B]$$
(2)

Where [B] is the anthraquinone concentration of anthraquinone/ethanol solution (g/L), Y is the corresponding absorbance value of anthraquinone/ethanol solution.

2) Determination of the solid acidity of TSANs

0.01 g of solid acid samples were added to 4 ml of cyclohexane solution, then 1 ml of 0.1 g/L of anthraquinone/ethanol solution as indicator was put in the above solution. After centrifuged, supernatant liquid was taken out, and the value of the absorbance of supernatant liquid was measured by ultraviolet spectrophotometer, with cyclohexane as the reference solution. According to the formula (2), the concentration of the anthraquinone in supernatant fluid [B] can be calculated with the absorbance value, then anthraquinone conjugate acid concentration in the supernatant [AB] was described as follows:

$$[AB] = 0.1/(4+1) - [B]$$
(3)

Finally, the solid acidity H₀ of TSANs were calculated by dragging [B], [AB] to formula (1). S2. Measurement of hydrophilic property of TSANs/PSF composite membranes

The hydrophilic property of membrane surface was evaluated by measuring water contact angles. Contact angles of different membrane samples were measured with an OCA20 dynamic contact angle measuring instrument (Dataphysics Corporation, Germany). Each sample was tested three times, and the average value of three results was taken as the contact angle of the sample membrane.

S3. Measurement of membrane anti-compaction ability

It is known that both membrane contamination and membrane compaction result in the flux declining of composite membranes. The negative effect of membrane contamination on the flux of membrane was removed by using membrane ultrafiltration water as the feed solution in this experiment. Thus, the anti-compaction ability of PSF membrane, SiO₂/PSF composite membrane, SZP/PSF composite membrane and TSANs/PSF composite membrane can be evaluated by the incrementation between membrane ultrafiltration water stable fluxes of membranes. Specific operation method and principle are similar to literature.¹ Permeation flux was calculated by the following equation:

$$J = \frac{V}{A \times t} \tag{4}$$

where J is the permeation flux (L m⁻² h⁻¹), V is the permeation volume (L), A is the effective membrane area (m²) and t is the operating time (h).

Then the incrementation between pure water stable fluxes of membranes was calculated by the following equation:

$$FI = \frac{J_t - J_{tp}}{J_{tp}} \times 100\%$$
(5)

where FI is the incrementation between membrane ultrafiltration water stable fluxes of membranes (%), J_{tp} is the membrane ultrafiltration water stable flux of PSF membranes (L/m²·h), J_t is the membrane ultrafiltration water stable flux of membranes (L/m²·h).

The pure water stable flux of membranes was determined by the the following equation:

$$\frac{J_{t-1} - J_t}{J_{t-1}} \times 100\% \le 2\%$$
(6)

where J_t is the membrane ultrafiltration water stable flux of membranes (L/m²·h), J_{t-1} is the previous point permeation flux before stable situation of membranes (L/m²·h).

References

1 Y. Zhang, Z. Jin, Y. Wang and P. Cui, J. Membr. Sci., 2010, 361, 113-119.