Supporting information

Plasma-assisted multi-layered coating towards improved gas permeation properties for organosilica membranes

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1. The schematic diagram of membrane fabrication

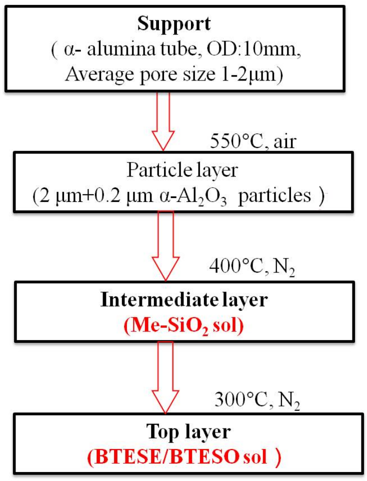

Fig. S1 The schematic diagram of membrane fabrication.

2. SEM images of organosilica membranes

Fig. S2 shows the SEM (FE-SEM, S-4800, HITACHI) images of four kinds of organosilica membranes. From the surface images, it can be observed that all of surfaces were smooth and defect-free with the exception of BTESE/Me-SiO_2 membranes. The inhomogeneous surface was confirmed by contact angles of BTESE sols coated on Me-SiO_2 layers (Fig. 5b). In the cross-sections of SEM images, the top and intermediate layers were difficult to distinguish for all the membranes, but the pore size of membranes was obviously reduced from bottom to top.

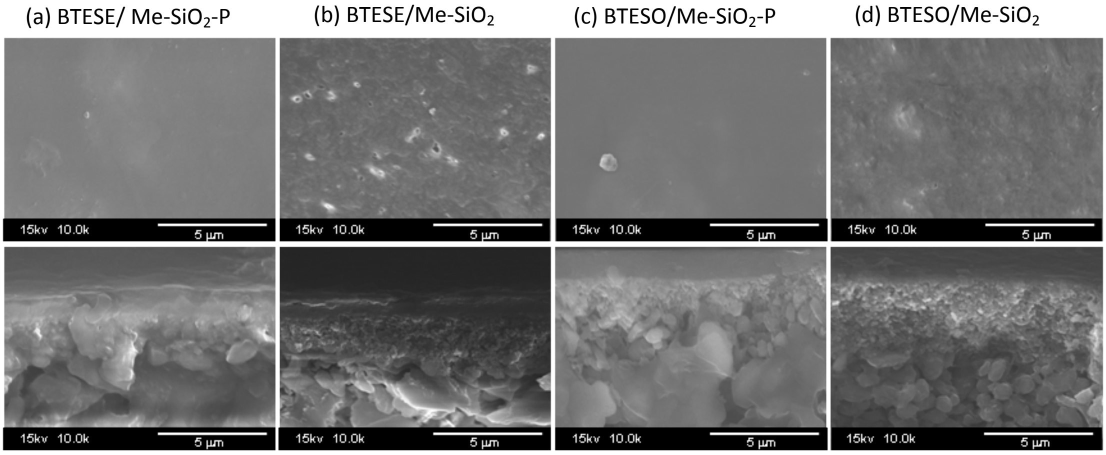

Fig. S2 SEM images of organosilica membranes with and without plasma treatment. (Up: surface; Down: cross-section)

2. The stability of organosilica membranes in the presence of water vapor

The hydrophobic organosilica membranes showed good stability in the presence of water vapor, as shown in Fig. S3. The permeance of CO_2 was constant for as long as 70 h under a feed stream that consisted of CO_2 gas saturated with water vapor.

In addition, the stability of BTESO/Me-SiO_2-P membrane was tested in water saturated with CO_2. The membrane was immersed in water through which CO_2 was bubbled under atmospheric pressure at 40 °C, and the permeance of CO_2 and H_2O were continuously measured. As shown in Fig. S4, the membrane showed a very stable performance for as long as 100 h.

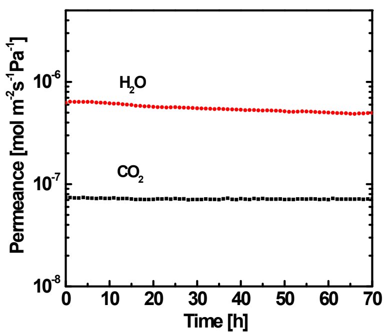

Fig. S3 Time course of CO_2 and H_2O permeance for BTESO/Me-SiO_2 membrane in the presence of water vapor at 40 °C

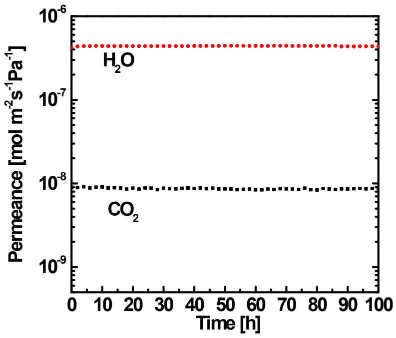

Fig. S4 Time course of CO_2 and H_2O permeance for BTESO/Me-SiO_2-P membrane in water at 40 °C.

3. The mechanism of gas transport through membranes

There are two main characteristic that dictate gas separation membrane performances: permeability and selectivity. Permeability is the gas flux permeation through the membranes. The ideal selectivity is defined by the ratio of the permeability of the individual component:

$$\alpha_{i/j} = P_i / P_j \qquad (1)$$

The schematic mechanism of gas transport is illustrated in Fig. S5. If the pore size of membranes is larger than 0.1 µm, gases transport through the membrane is by convective flow and no effective separations occur. When the pore diameter is in the range of 1-50 nm, comparable to or smaller than the mean free path of the gas molecules, the diffusion is governed by Knudsen diffusion. The selectivity is in inverse proportion to the square root of its molecular weight. When the pores of porous membrane are on the order of sub-nanometers, then gases are separated by molecular sieving. Gas molecules with a diameter that is smaller than the pores of a membrane can be transported through the membranes while gas molecules with a larger diameter would be prohibited. In the case of surface diffusion, gas molecules adsorb on the pore walls, and diffuse along the adsorption gradient. For capillary condensation, as an extension of surface diffusion, the low pressure of vapor in the micropores causes vapor condensation, which prohibits the other gases through membranes. The solution-diffusion mechanism is used to describe polymer membranes.

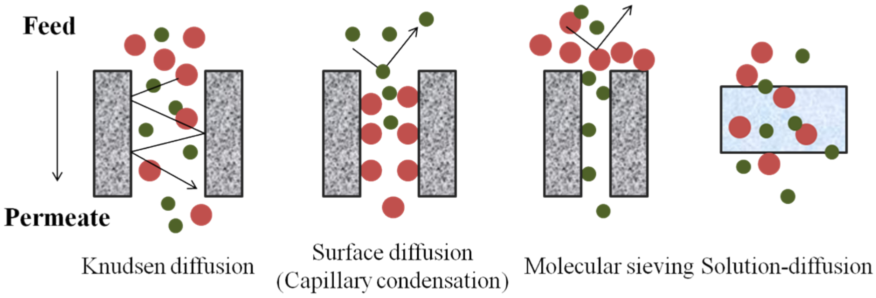

Fig.S5 Schematic diagram of the mechanism of gas transport through membranes.

In this work, two types of hybrid silica membranes, BTESE and BTESO, showed different properties and gas separation mechanisms, due to structural differences (BTESE: Si-$(CH_2)_2$-Si; BTESO: Si-$(CH_2)_8$-Si). By characterization of N_2 adsorption isotherms, BTESE showed microporous structure and BTESO showed nonporous structure due to long organic chains, which was reported in our previous work.[15] Therefore, for BTESE membrane, gas transport is based on the surface diffusion or molecular sieving. On the other hand, gas through BTESO membrane is based on a solution-diffusion mechanism.