

Electronic Supplementary Information

Dual-Functionalized Mesoporous TiO₂ Hollow Nanospheres for Improved CO₂ Separation Membranes

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Experimental

Materials

Potassium titanium oxide oxalate dehydrate (PTO, technical, $\geq 90\%$ Ti basis), poly(ethylene glycol) (PEG, $M_n = 400$ g/mol), poly(vinyl chloride) (PVC, $M_n = 99,000$ g/mol), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, $M_n = 475$ g/mol), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA, 99%), copper(I) chloride (CuCl, 99%), poly(ethylene glycol) diglycidyl ether (PEGDE, $M_n = 500$ g/mol), and (3-aminopropyl)trimethoxysilane (APS, 97%) were purchased from Aldrich. All chemicals were reagent grade and were used as received.

Synthesis of PVC-g-POEM graft copolymer

PVC-g-POEM graft copolymer was synthesized through a typical ATRP procedure. First, 6 g of PVC was dissolved in 50 ml of NMP by stirring at room temperature for 1 day. After stirring, 0.10 g of CuCl was added, and then 24 ml of POEM was added. Subsequently, 0.24 mL of HMTETA was immediately added to the solution. Then, the green mixture was purged with nitrogen for 30 min. The reaction was carried out at 90 °C for 24 h. After polymerization, the resultant mixtures were precipitated into methanol three times. Products were dried in an oven at 50 °C overnight. Then, they were dried again in a vacuum oven overnight at room temperature.

Synthesis of mesoporous TiO₂ hollow nanosphere (MTHS)

First, 0.266g of PTO was dissolved in 45 mL of water and was stirred for 2 h. Then, 22.5 ml of PEG was added into the PTO solution and was stirred for 30 min. The mixture solution was transferred to an autoclave and kept at 180 °C for 15 h; then, the autoclave was cooled

naturally in air. The product was harvested by centrifugation, followed by washing three times with water and ethanol to remove residual unreacted reagents. After being dried overnight in an oven at 50 °C, the samples were calcined at 500 °C for 30 min in order to remove the residual organics.

Synthesis of dual-functionalized mesoporous TiO₂ hollow nanosphere (f-MTHS)

First, 0.4g of MTHS was dispersed in 90 ml of toluene, and then 6 ml of APS was added to the solution. The reaction was carried out at 60 °C for 6 h. The product was collected by centrifugation, followed by washing three times with ethanol to remove residual APS. The amine-functionalized MTHS was dried in an oven at 50 °C and then cured at 120 °C for 2h. Second, the amine-functionalized MTHS was dispersed in 80ml of a 10 v/v% PEGDE solution in toluene. The reaction was carried out at 80 °C for 8 h. Product was harvested by centrifugation, followed by washing three times with water to remove residual PEGDE in the product. Then, the product was dried in a vacuum oven overnight at 50 °C.

Preparation of MMMs

Four kinds of MMMs were fabricated with different f-MTHS weight percents of 0, 10, 20 and 30 wt%. For a better comparison of the membrane mechanical properties with diverse polymer to THS ratios, the total amount of components was fixed to 0.3 g. PVC-g-POEM solutions and THS solutions with different ratios were separately dispersed in THF. The dispersed THS solution was slowly added to the polymer solution. After sufficient mixing using sonication and stirring, the PVC-g-POEM/THS solution was cast onto Petri dishes. After air drying at 50 °C for 3 h, the films were removed from the dishes. The films were stored under vacuum in an oven at room temperature for another 24 h to assist in the removal

of the residual THF and adsorbed water. The thicknesses of the membranes were in the range of $70 \pm 5 \mu\text{m}$.

Permeability Measurements

The pure gas permeation properties were determined using a constant volume/variable pressure apparatus provided by Airrane Co. Ltd. (Korea). The leak rate in the system was measured before starting the permeation experiments; afterward, the pressure increase in the downstream volume was recorded to determine the permeability. The gas permeability was calculated from the steady-state rate of the pressure increase in a fixed downstream volume. The downstream pressure was always less than 20 mmHg, which is very low compared to the upstream pressure (800 mmHg).

Characterization

The morphologies of the THS and PVC-g-POEM/THS mixed matrix membranes (MMMs) were observed using a field-emission scanning electron microscope (FESEM, SUPRA 55VP, Germany, Carl Zeiss), and transmission electron microscope (TEM) images were obtained using a JEOL JEM 1010 microscope operating at 300 kV. For the TEM measurements, the THS powder was dispersed in a solvent such as ethanol; then, a drop of this solution was placed onto a standard copper grid. The specific surface area and pore size diameter were determined from N_2 adsorption–desorption measurements by applying the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. In advance of these measurements, the samples were additionally degassed at 70°C under a dynamic vacuum (1×10^{-2} Torr) for 1 h. The amount of PEGDE attached on the THS surface was analyzed by TGA measurement.

Figure S1. TGA curve of f-MTHS.

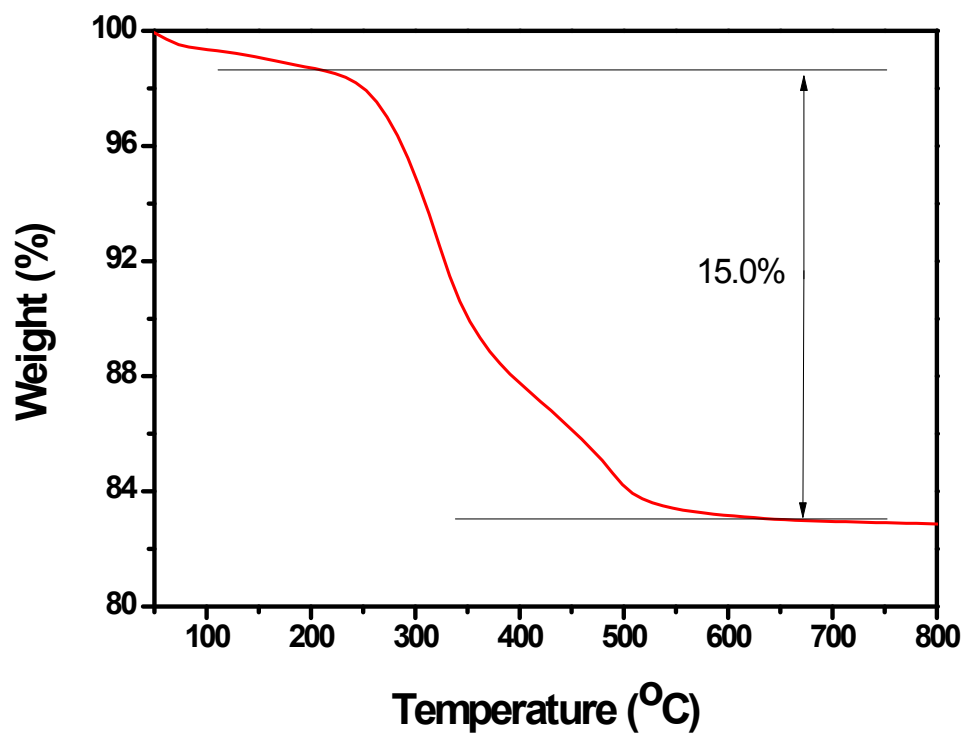


Figure S2. N₂ adsorption-desorption curves of MTHS and f-MTHS.

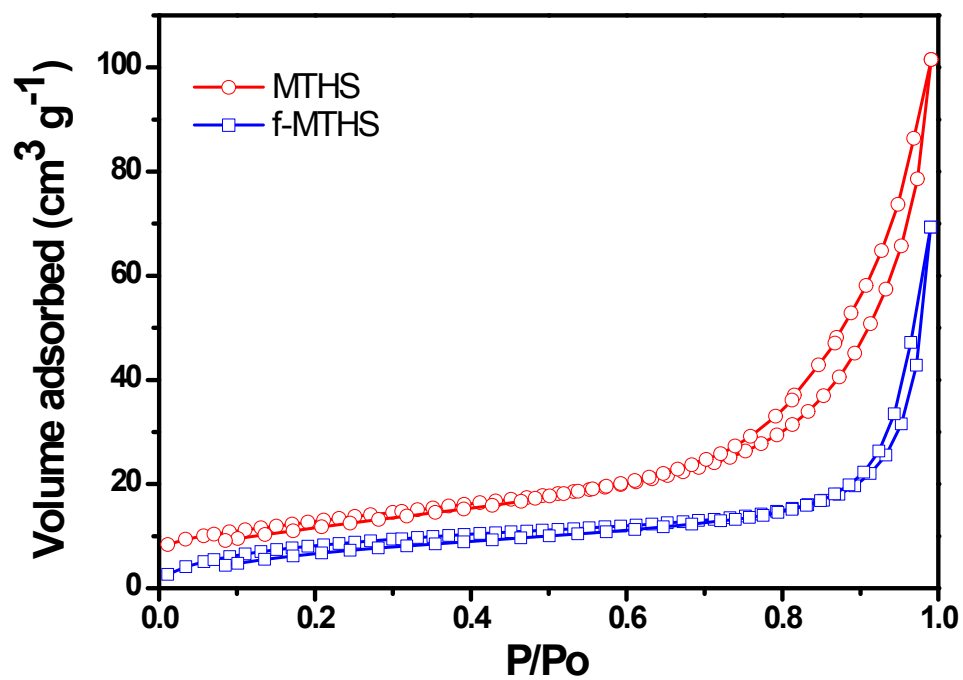


Figure S3. Cross-sectional SEM image of MMM with 20wt% f-MTHS.

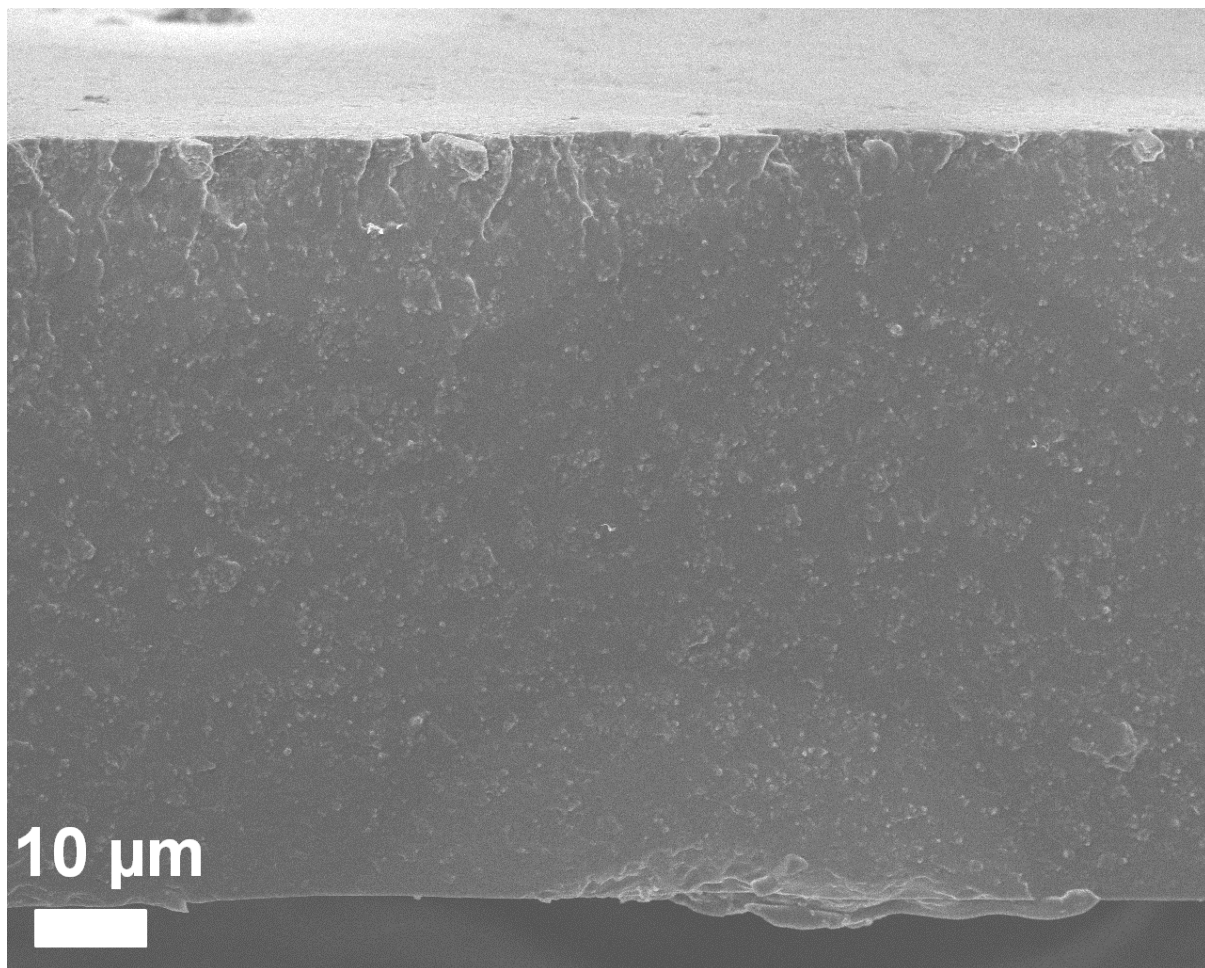


Figure S4. Photos of MMMs with f-MTHS contents of (a) 0 wt%, (b) 10 wt%, (c) 20 wt% and (d) 30 wt%.

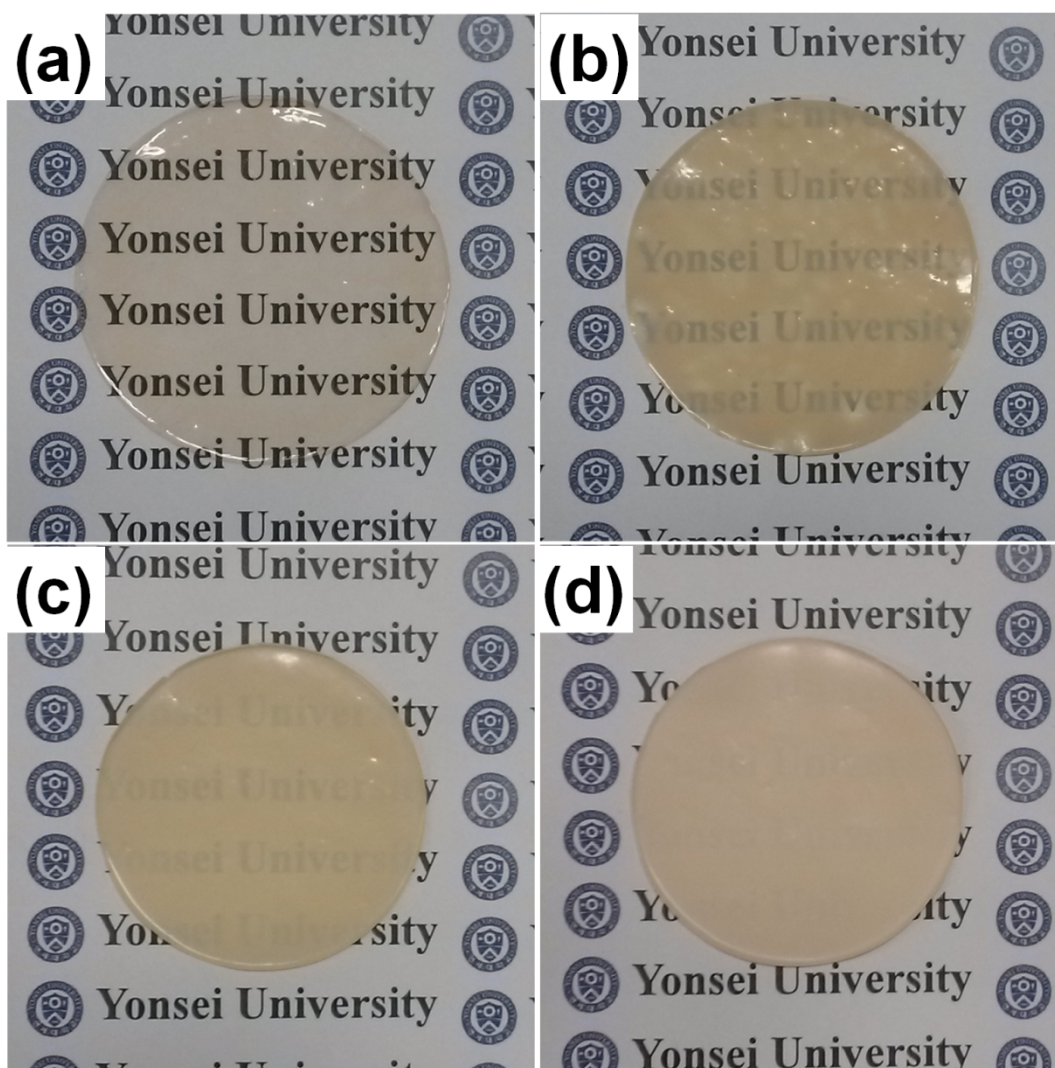
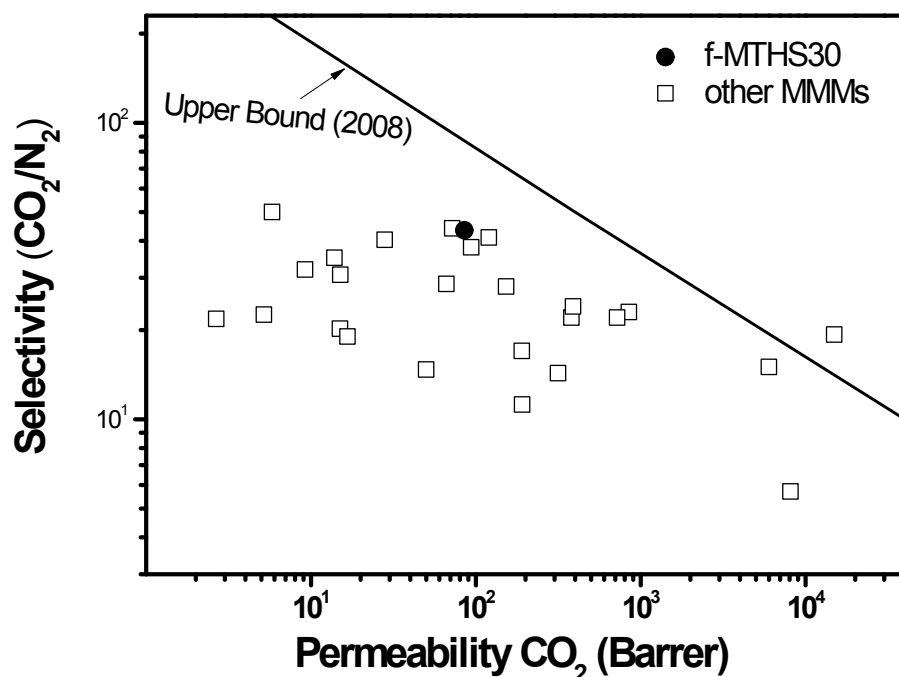


Figure S5. Relation between CO₂ permeability and CO₂/N₂ selectivity of PVC-g-POEM MMM containing f-MTHS 30wt% (black solid circle), compared with the previously reported data on MMMs (black open squares)¹⁻⁹. The upper bound for polymer membrane performance defined in 2008 is shown¹⁰.



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