

Supplementary information

Relationship between surface hydrophobicity and flux for membrane separation

Gil-Seon Kang,^a Youngbin Baek^{b*} and Ji-Beom Yoo^{c*}

Experimental section

Fabrication of hydrophilic AAO membranes

The AAO membranes of the highly self-ordered nano-pores arrays were prepared by a two-step anodizing method. High-purity aluminum foils (99.999 %, 0.25 mm thickness, Good-fellow) were used without an annealing step. The Al foils were electrochemically polished in a 1:4 mixture solution of perchloric acid (60%, Junsei) and ethanol (98%, J.T. Baker) for the smooth and uniform surface. Maintaining the temperature of 15 °C, the electro-polishing was performed at 100 mA/cm² for 5 min to obtain a mirror-like shiny surface [1]. Then, the anodizing process was carried out in 0.3 M oxalic acid solution (H₂C₂O₄, Sigma-Aldrich) using the graphite plate as the cathode. The temperature of the solution was maintained at 5 °C, and the potentiostatic voltage was at 40 V for 12 h. After the first anodizing step, the randomly formed porous alumina was removed by wet chemical etching with a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid at 60 °C. Afterwards, the second anodizing step was immediately carried out under the same condition as the first step, with a longer duration of 24 h. The remaining non-anodized Al substrate was removed by a reaction with 100 mL of H₂O + 3.4 g of copper (II) chloride dehydrate and 100 mL of hydrochloric acid. The oxide barrier layer was subsequently opened by 0.1 M phosphoric acid at 35 °C [2]. Pore widening was performed after the removal of barrier layer, using 0.1 M phosphoric acid for the desired time to achieve the required pore dimensions.

Fabrication of hydrophobic carbon-coated AAO (C-AAO) membranes

AAO membranes with different pores diameters ranging from 40 to 80 nm and a thickness of 70 μm were used for uniform carbon coating on the inner wall of the AAO membranes by non-catalytic chemical vapor deposition (CVD) [3]. Polycrystalline AAO membranes were obtained by transformation from amorphous to γ -alumina above 850°C [4], and the pyrolysis of acetylene at a temperature ranging from 500 to 1,000°C had been conducted to coat the inner wall of AAO membranes. It was found that carbon was not deposited without catalyst below 700°C. The AAO membranes were slowly heated up to 800 °C with the heating rate of 10°C/min because of the different thermal expansion coefficient between Al_2O_3 [5] and carbon [6], under a mixture of C_2H_2 [7, 8] and Ar gases, and the working pressure was 2.88 Torr. The temperature, working pressure and carbon precursor were maintained at the same condition for 50 min followed by that carbon coated AAO (C-AAO) membranes were slowly cooled down at room temperature with the cooling rate of 5 °C/min.

O₂ plasma surface treatment of C-AAO membranes

The surface energy of C-AAO membranes were changed from hydrophobic surface to hydrophilicity regardless of energy of pore surface. This could control the thickness of the graphite crystalline form of the element carbon by oxygen plasma etching [9], so that we can easy removed the amorphous carbon surface of the C-AAO. The O₂ plasma treatment was 50 sccm of oxygen gas and the plasma power was 100 W. Treatment time was approximately 3 – 10 min according to the etching rate of nanometer-thick graphite film was ~0.23 nm/min

CuO molecules synthesis

A mixture solutions of 30 mL of 0.014 M ascorbic acid ($C_6H_8O_6$, Sigma-Aldrich) and 200 mL of 1 M Sodium hydroxide (NaOH, Samchun) was added into 1.265 mL of 0.3 M copper (II) acetate ($Cu(Ac)_2$, Sigma-Aldrich) solution at room temperature. When the mixed solution is stirred for 30 minutes, it turns yellow and becomes turbid to form Cu_2O . And then, the precipitates were collected and washed by centrifugation [10]. After vacuum dried at $60^\circ C$ overnight, the collected Cu_2O molecules powders were further calcinated using box furnace at $410^\circ C$ for 6 hours ($1^\circ C/min$) to get CuO molecules. Finally, aggregated CuO was separated using a tip sonicator due to filtration, and dispersed CuO molecules size was confirmed by DLS.

Filtration Experiments

The flow velocities of AAO and c-AAO membranes were performed to investigate the effect of the surface chemistry of the pores on the performance of membrane depending on pore diameters. The water fluxes were measured using dead-end filtration and applied pressure was 2 bars. Permeate solution was collected and weighed. Flux was calculated from the information on permeate volume (mL), time (min) and total membrane area (cm^2). The water flux of the membranes with the hydrophilic surface can be predicted by Hagen-Poiseuille equation (Eq. 1), assuming no-slip between a solid (inner wall of AAO) and a liquid (water).

$$Q_{HP} = \frac{\left(\frac{D}{2}\right)^4 \cdot \Delta P \cdot \pi}{8 \cdot \mu \cdot L} = \frac{D^4 \cdot \Delta P \cdot \pi}{128 \cdot \mu \cdot L}$$

(1)

where Q_{HP} is the theoretical volumetric flow rate, D is the pore diameter (40 – 80 nm), ΔP is the applied pressure (2 bar), μ is the dynamic viscosity of solution, and L is the length of the membrane thickness (70 μm). Note that membrane size was 0.5 cm^2 approximately and pore density was $1.02 \times 10^{10} / \text{cm}^2$ for all types of membranes. The flow enhancement factor is the conventional method to discuss the water flow enhancement on a hydrophobic surface. The flow enhancement factor ε , is described by Eq. 2 and calculated from the ratio of the experimental flux to the theoretical flux obtained by Eq. 1. The change of viscosity by pore diameter was ignored, because the pore diameter is sufficiently larger than the interface dimension between water molecules and inner wall [18].

$$\varepsilon = \frac{Q_{exp}}{Q_{HP}} = 1 + 8 \frac{L_s}{D} \quad (2)$$

where Q_{exp} is the volumetric flow rate from measurement, and L_s is the slip length to show the differences between theoretical flow (Q_{HP}) and the actual flow (Q_{exp}) [19].

CuO nanoparticle with 64 nm of hydrodynamic diameter was used to evaluate the rejection properties of AAO, C-AAO, O₂ C-AAO membranes. Concentration of CuO solution was 16 mg/L and applied pressure was same as previously (i.e. 2 bar). Rejection rate was calculated as follows.

$$R_{exp} = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100\% \quad (3)$$

where R_{exp} is the experimental rejection rate (%), C_{feed} is the feed concentration of CuO solution (16 mg/L) and $C_{permeate}$ is the concentration of CuO in the permeate, measured by both weighing residual amounts after filtration and drying.

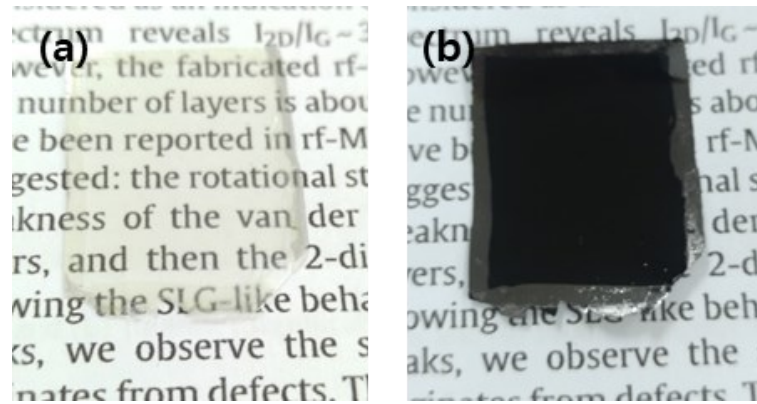
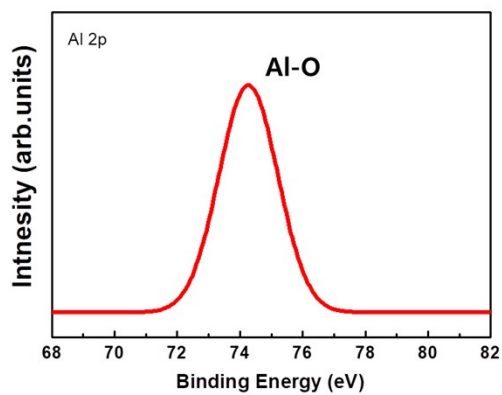


Fig. S1. Digital pictures of (a) AAO membrane and (b) C-AAO membrane

(a) AAO



(b) c-AAO

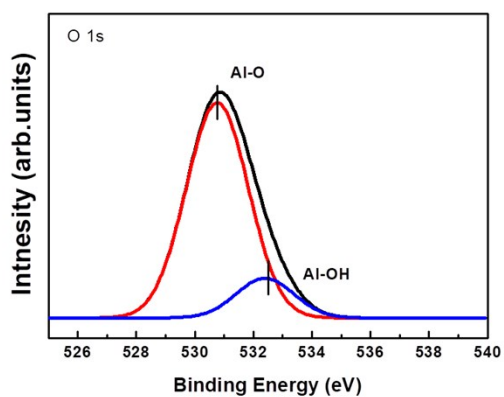
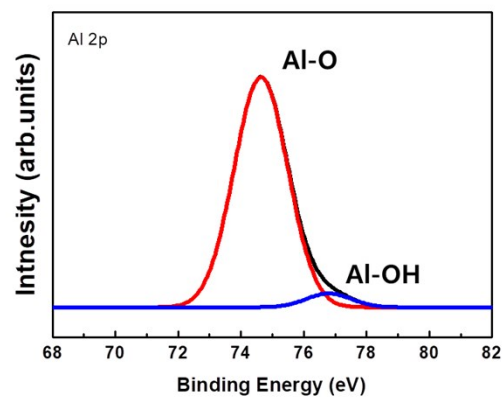


Fig. S2. The XPS of AAO spectrum had Al-O bonds at Al 2p and O1s. When Al_2O_3 was formed, it was confirmed that the Al-OH of O1s was terminated by hydrogen bonding to the surface. However, the Al-OH peak of Al 2p means unstable oxygen bonds with hydrogen due to carbon and oxygen bonding in c-AAO.

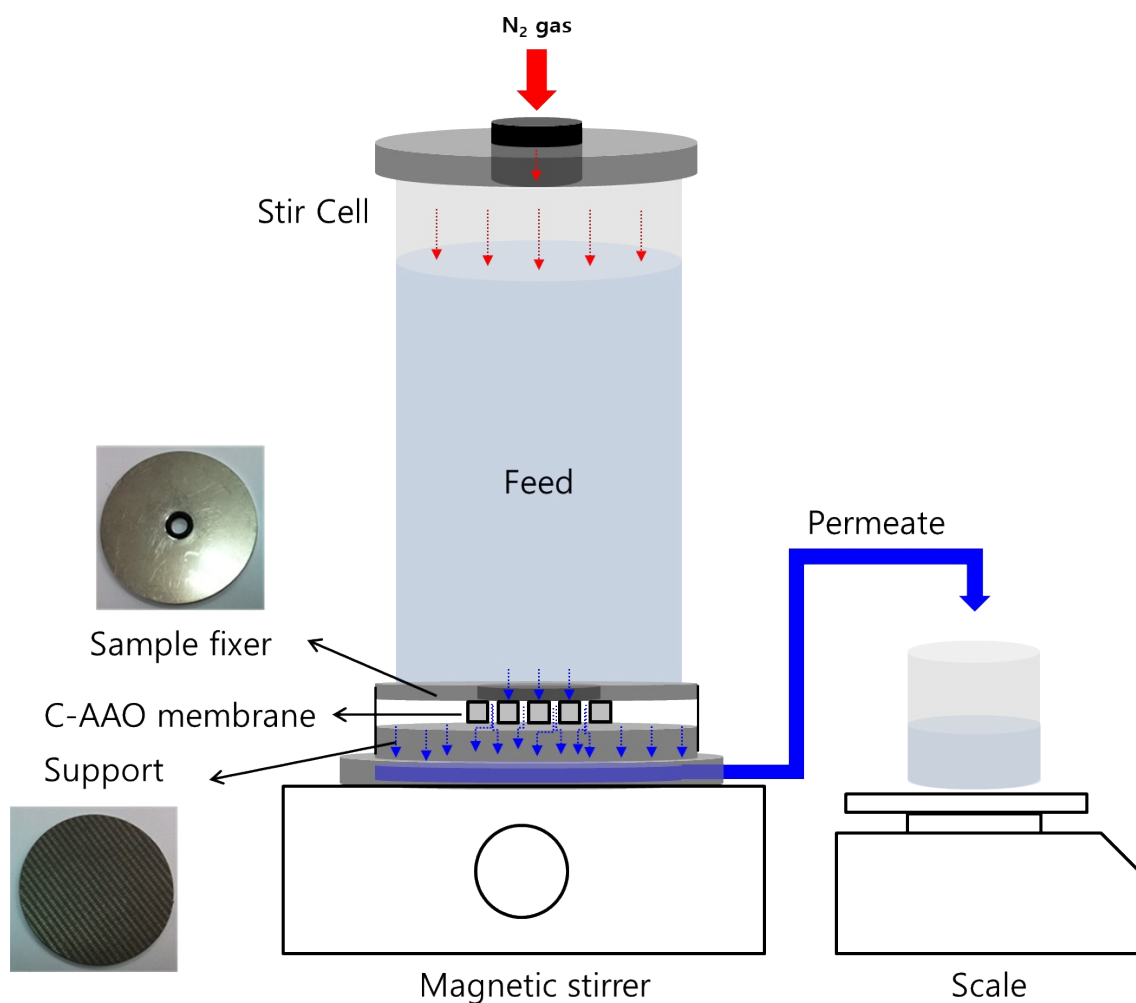


Fig. S3. Schematic of dead-end filtration system. Membrane samples were equipped between sample fixer and support to use effective membrane area. N₂ gas was applied at 2 bar and permeate was weighed to calculate flow velocity.

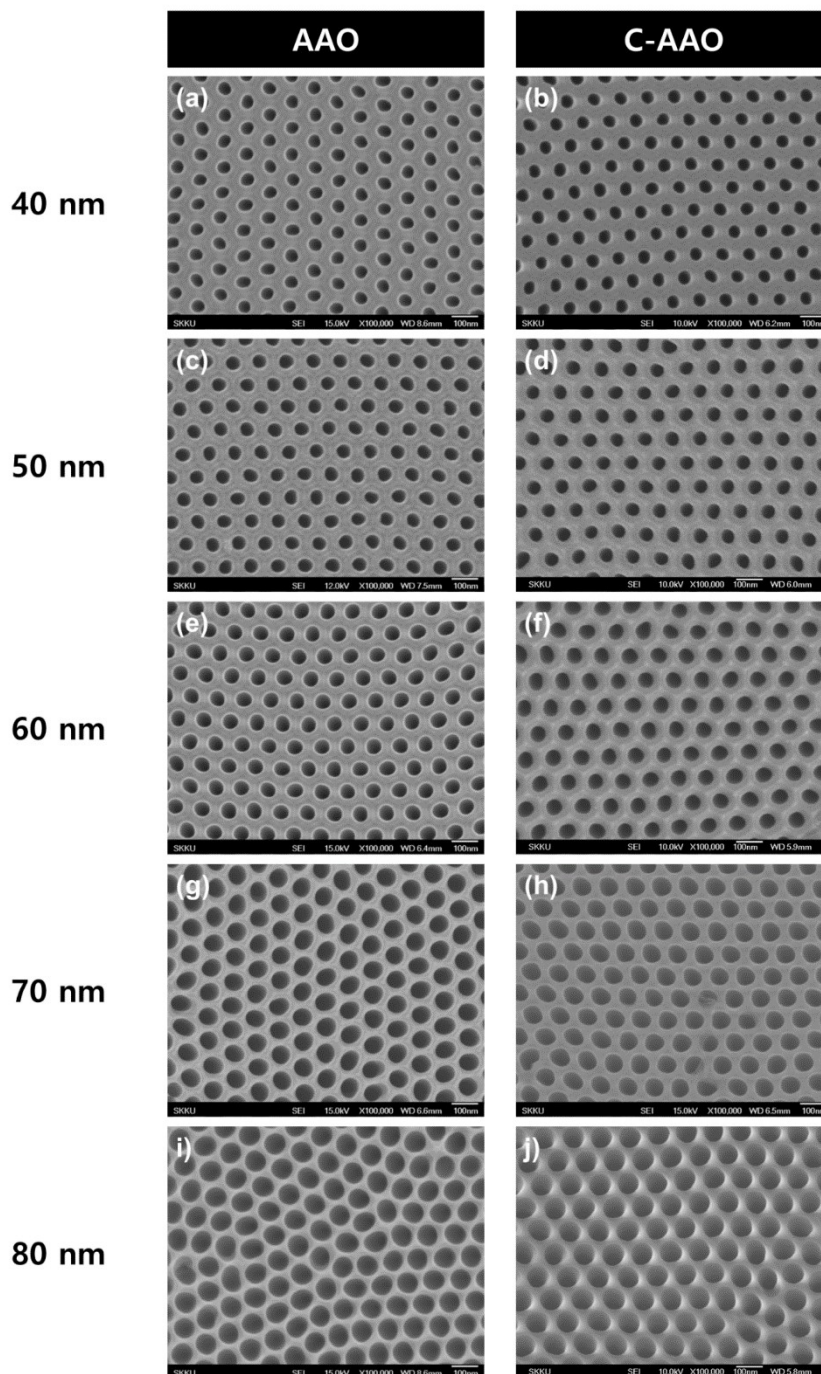


Fig. S4. SEM images show different pore sizes of AAO and carbon-coated AAO membrane. The pore size of the AAO membrane was controlled from (a) 40 nm to (i) 80 nm. After uniform carbon coating on the inner wall of the AAO membrane by CVD, the images of c-AAO membrane was also shown in (b) to (j). The pore size differences were not observed in the SEM images.

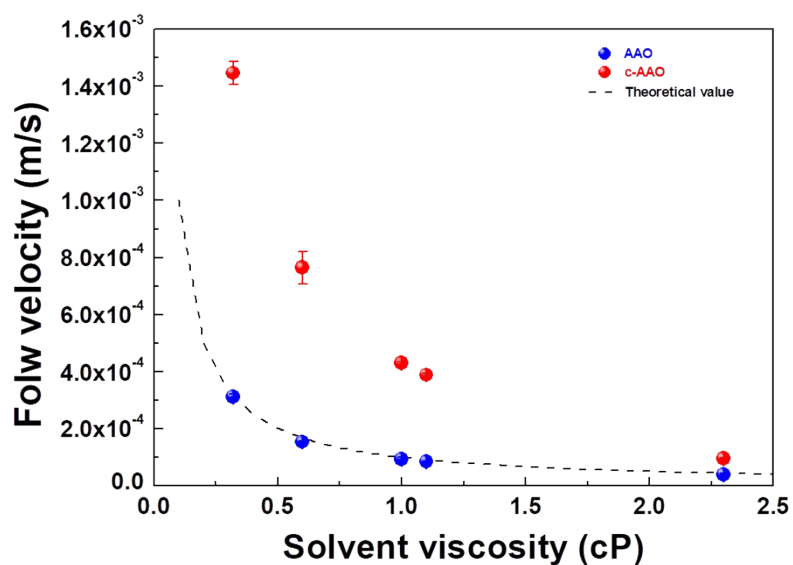


Fig. S5. Flow velocities of AAO and C-AAO membranes with various solvents; acetone (0.32), methanol (0.6), water (1), ethanol (1.1), IPA (2.3). The blue dot is flow velocity of hydrophilic surface (AAO membrane), and the red dot of hydrophobic surface (C-AAO membrane) by experimental solvent velocity. The theoretical flow velocity (black line) was calculated from eq(1).

S6

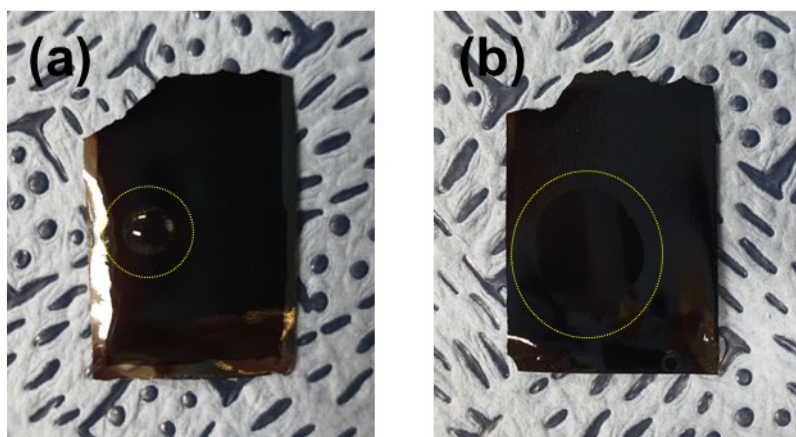


Fig. S6. Digital pictures of (a) C-AAO membrane and (b) O₂ plasma treatment C-AAO membrane

S7

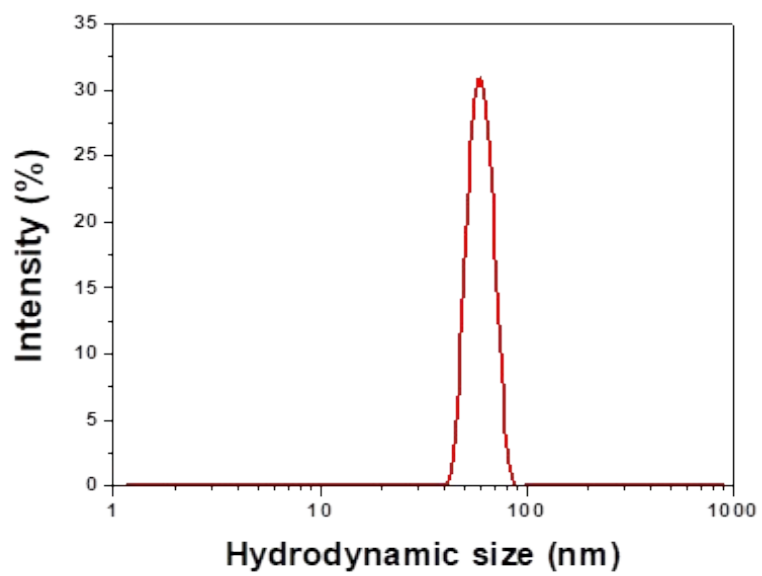


Fig. S7. Dynamic light scattering results for CuO solution.

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