Supporting Information

Enhanced Water Permeation Based on Nanoporous Multilayer Graphene Membrane: The Role of Pore Size and Density

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Figure S1. (a), (c), (e) X-ray diffraction spectra of Pre-G, AG and AGO depending on the degree of pre-oxidation. The numbers indicate the ratio of $KMnO_4$ used for pre-oxidation of 1g graphite. (b), (d), (f) D/G ratio of Raman spectra of Pre-G, AG and AGO depending on the degree of pre-oxidation.

To investigate the variation of the interlayer of graphite samples and the defect structures depending on each preparation step, X-ray diffraction (XRD) spectroscopy and Raman

spectroscopy was carried out on pre-oxidized graphite, activated graphite and functionalized graphite as shown in **Figure S1**.

Figure S1a shows the increased interlayer distance of pre-oxidized graphite sample depending on the weight ratio of $KMnO_4$ to graphite. While graphite displays a sharp (002) peak at 26.5° (d-spacing ~ 3.36 Å), the peak shifts to a lower angle as the amount of KMnO₄ increased. An additional shoulder peak appears at 25.8° (d-spacing ~ 3.45 Å) in Pre-G 0.1. Peaks were observed near 10.6° (d-spacing ca. 8.37 Å) from Pre-G 2 and at 9.54° (d-spacing ca. 9.26 Å) from Pre-3.5 due to the decoration of carboxyl and hydroxyl groups on the basal plane of graphene.¹ Because the oxidation of graphite using KMnO₄ is initially involves formation of epoxide groups, the increase of d-spacing to 3.45 Å in Pre-G 0.1 can be attributed to the decoration of graphene plane with epoxide group rather than other oxygen containing functional groups. Pre-G samples except for Pre-G 3.5 have interlayer spacing of graphite, corresponding to the sharp peak at 26.5° (d-spacing ca. 3.36 Å) (Figure S1c), because functional groups were decomposed during KOH activation at a temperature of 800 °C. Because Pre-G 3.5 is excessively oxidized, its graphitic structure of graphene is highly distorted, resulting in the disappearance of (002) peak from interlayer of graphite. In order to functionalize the activated graphite (AG), the conventional modified Hummer's method was used regardless of degree of pre-oxidation. The peaks from AGO to AGO 0.1 appeared at near 10° (d-spacing ca. 8.26 Å - 9 Å) like that of typical graphene oxide and owing to the existence of oxygen-containing functional groups (Figure S1e). On the other hand, clear diffractions corresponding to (002) peak are not observed in AGO 2 and AGO 3.5.

Raman spectroscopy (**Figure S1b**) confirmed that increased oxidation of graphite occurs depending on the weight ratio of KMnO₄ to graphite during pre-oxidation. The D band / G band ratio of Raman spectra increased from ca. 0.1 of graphite to 1.0 of Pre-G 3.5, indicating the enhanced degree of defects and amounts of sp³ bonds.¹ After activation, the D band / G band ratio was reduced to that of graphite in the case of AG 0.1 and AG 0.5, reconfirming the decomposition of oxygen functional groups during KOH activation. The remaining high D band / G band ratio of AG 2 and AG 3.5 can be attributed to the decomposition and destruction of the structure of graphite by the excessive gasification of sp³ carbon during KOH activation. D band / G band ratio from all functionalized graphite samples increased again, because sp³ bonds are formed by functional groups during hummer's method.



Figure S2. (a), (c), (e) XPS spectra of Pre-G, AG and AGO depending on the degree of preoxidation. (b), (d), (f) FT-IR spectra of Pre-G, AG and AGO corresponding to (a), (c) and (e), respectively.

X-ray Photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) spectroscopy were used to detect the composition of elements and functional groups (**Figure S2**). In **Figure S2a** is shown increasing intensity of shoulder peaks of C1S spectra at 286.8 eV depending on

the degree of pre-oxidation. A peak for C-O (at 286.8eV) was not observed in graphite but begins to appear as graphite is pre-oxidized from Pre-G 0.1 to Pre-G 3.5. With more KMnO₄, the intensity of the peak corresponding to C-O gradually increases. The spectrum of fully oxidized graphite (Pre-G 3.5), which was prepared by using the general Hummer's method shows several additional several peaks including C=O (287.8 eV) and O=C-O (289 eV).² Similar oxidation tendency was observed in a FTIR investigations (Figure S2b). Although graphite does not show particular absorbance peaks, the absorption peak of epoxide bond at 1032 cm⁻¹ appears in the spectrum of Pre-G 0.5. The intensity of absorption peaks at 3354, 1722, 1617, 1211 and 1032 cm⁻¹, which are attributed to stretching vibrations of the respective O-H, C=O, C=C, carbonyl C-O and epoxide C-O bonds, increase with higher degrees of oxidation.² Both the XPS and FTIR results show that few oxygenated functional peaks are present after KOH activation at 800 °C (Figures S2c and S2d), because oxygen functional groups are decomposed during the KOH activation at high temperature. However, inspection of Figures S2e and S2f shows that oxygen functional groups reappear after functionalization. Although general graphene oxide peaks are observed in the FTIR spectra of AGO and AGO 3.5, the shape and intensity of XPS C1S peaks of other AGO samples are significantly different from those of AGO 3.5, showing much smaller shoulder peaks for C-O in AGO 3.5 (Figure S2e). It seems that oxidization of AG 3.5 is relatively difficult due to the restructured carbon during the KOH activation. The effects of KOH activation on the structure of highly oxidized graphene is described below.





Degree of pre-oxidation

Figure S3. SEM images of AG and AGO depending on the degree of pre-oxidation. 2D shape of graphite was well preserved during the activation and functionalization in the graphite samples with low degree of oxidation (AG, AG 0.1 and AG 0.5). On the other hand, AG 2 begins to show the slight degradation of 2D graphite and a significant increase of macroscopic porous structures was observed even in AGO 3.5 sample. All scale bars are 10 µm.



Figure S4. Effects of pre-oxidation on the dispersion and exfoliation of AGO. (a) Photographs of dispersions of AGO ($0 \sim 3.5$) in water with the concentrations of 0.1 mg/mL. Dispersions were well obtained from AGO to AGO 0.5. AGO 2 whereas AGO 3.5 usually precipitated in the form of large particles. (b) SEM image of AG 3.5 after activation. A complex three dimensional pore structure was observed rather than maintaining 2D sheet. (c) TEM image of

AG 3.5. Three dimensional micro and mesopores were commonly observed, because abundant defective structures in Pre-G 3.5 are highly reactive during KOH activation, resulting in degradation of defective carbons.



Figure S5. (a) High resolution TEM image of graphite. **(b)** and **(c)**, Magnified ultrahigh resolution TEM images of graphite and configuration showing the perfect hexagonal structure of carbon atoms.



Figure S6. (a) Low magnification of dispersed activated graphite without pre-oxidation. Inset is a SAED pattern obtained from corresponding graphite flake. **(b)** TEM image showing the edge of activated graphite without pre-oxidation. Insets are contrast profiles along the arrow indicating the locally expanded interlayer space of activated graphite and TEM image showing the edge structure of normal graphite. Schematic illustration describes the structural variation of graphite during KOH activation. **(c)** HR-TEM image of the basal plane of AG without preoxidation. Representative defect regions are marked with yellow dotted circles. Insets are the FFT images and distributions of vacancy defects with respect to the number of missing carbon

atoms in a 2000 nm² area. (d) Magnified ultra-HR-TEM images of graphite without activation. (e) Magnified ultra-HR-TEM images of AG without pre-oxidation, showing the vacancy regions where several carbon atoms are missing.

To verify the role played by KOH activation in generating the atomic vacancy defects on the basal plane of graphene, we carried out ultra-high-resolution transmittance electron microscopy (HR-TEM) before and after KOH activation of graphite using an FEI Titan TEM equipped with two Cs correctors, a monochromator, and a brightness electron gun at 80 kV (Figure S6). Inspection of the edge of the TEM image of the KOH-activated graphite reveals a highly modified and waved interlayer of stacked graphene, confirming the generation of surface defects and a disconnected plane of graphene with atomic pores (Figure S6a and S6b). The carbon atoms of unactivated graphite are perfectly arranged in the defect-free hexagonal structure, which shows hexagonally packed hexagons with dark regions due to the contrast of transmitting electrons at the carbon atoms (Figure S5 and Figure S6). Meanwhile, the hexagonal crystalline structure was confirmed by observing the sharp hexagonal peak in the fast Fourier transform (FFT) spectrum (inset of Figure S6c); defect regions where carbon atoms were missing were clearly observed after KOH activation, as indicated by yellow dotted circles in Figure 6Sc. Various vacancy defects at atomic resolution are more clearly visible in the magnified ultra-HR-TEM images (Figure 6Se). Boundaries of vacancy defects are marked with red lines in corresponding configurations. Interestingly, these atomic vacancy defects are simply formed by extracting a few carbon atoms (1-4) in the original hexagonal lattice of graphene while the sp² bonding of carbons were maintained. The distribution of vacancy defects generated by KOH activation was determined by counting 51 defects in a 2000 nm² area (inset of Figure S6c). Vacancy defects missing 1-3 carbon atoms (>85%) were most common, and defects missing >5 carbon atoms and nano-sized pores are rarely seen in the TEM investigations. We attribute the generation of atomic vacancy defects in graphene by KOH activation to the high chemical stability of graphene. Because gasification of carbon atoms easily occurs in sp³-bonded carbon rather than in sp²-bonded carbon, chemical activation of graphite crystal is very difficult.^{1,3,4} Thus, carbon atoms in graphene are extracted during KOH activation rather than forming the three dimensional nano-sized pore structure as in the case of GO,⁵ coals,⁶ and carbon fibers.⁷



Figure S7. AFM images of exfoliated GO, AGO, AGO 0.1 and AGO 0.5. The heights of all samples are 1 nm, indicating the exfoliation of functionalized single layer sheets.

Atomic force microscope (AFM) images and the height profiles confirmed the single layer characteristics of GO, AGO, AGO 0.1 and AGO 0.5, showing well exfoliated graphene sheets with ca. 1nm thickness (**Figure S7**).⁸ The size of flakes usually is in the several micrometer range.



Figure S8. AFM image of AG dispersed in DMF and a height profile obtained from white dotted lines in the AFM image. AG was exfoliated by sonicating AG powder in DMF solution, followed by centrifugation to remove the unexfoliated flakes. A diluted AG solution was dropped on SiO₂/Si and dried at room temperature. Although the AG solution was centrifuged at 10000 rpm, the degree of exfoliation was poor showing the multilayer graphene around 5 nm. Thin graphenes were also observed, but the size of flake was several hundred nanometer. Thus AG is not proper to fabricate the nano film without cracks for membrane application. It seems that additional exfoliation techniques are required to fabricate the graphene membrane with AG.



Figure S9. Photograph and SEM images of exfoliated AG filtrated using AAO. While AG can be dispersed in DMF and other proper solvents by sonication and separated by centrifugation, its size is submicron and it is usually composed of stiff multi-layer sheets, which are not proper to prepare the defect-free nano film in large area. Thus, many vacancy regions were observed in the AG film.



Figure S10. TEM images of GO, AGO without pre-oxidation, AGO 0.1 and AGO 0.5. Nanopores are marked with yellow dotted circles in each TEM image. While nano-pores are not observed in GO and AGO without pre-oxidation, AGO 0.1 and AGO 0.5 samples show nanopores on the basal plane of the graphene surface. Especially, the density of nano-pores significantly increased in the case of AGO 0.5, indicating that the degree of oxidation is highly responsible for the density and size of nano-pores generated by KOH activation.



Figure S11. (a) and **(b)**, HR-TEM images of GO and AGO without pre-oxidation. **(c)** and **(d)**, Magnified HR-TEM image of GO and AGO without pre-oxidation.

While same oxidation processes were conducted for both GO and AGO without pre-oxidation, the HR-TEM images of GO and AGO without pre-oxidation show that the degree of oxidation is obviously different. Larger sp² domains are maintained in AGO rather than GO (**Figures S11a** and **S11b**). **Figure S11c** contains a magnified HR-TEM image of GO, showing its complex pore structure. Nanopores around 2 nm were occasionally observed as marked with red dot lines and micropores were also observed in the amorphous carbon regions rather than sp² domain regions, indicating that generation of small amounts of nanopores are induced by the chemical oxidation via Hummer's method. In contrast, many vacancy defects marked with

yellow dot circles are observed in well maintained sp² domain and nano pores are rarely observed in AGO withour pre-oxidation (Figure S11d).



Figure S12. Pure water flux of AGO membranes depending on the applied pressure.

Pure water flux of AGO membrane depending on the applied pressure was also investigated as increasing the pressure from 2 bar to 10 bar as shown in **Figure S12**. Water flux linearly increased as increasing the pressure in the range of our experimental condition.



Figure S13. Schematic illustration of the membrane equipment used for the desalination test.



Figure S14. XRD spectra of GO and AGO membranes fabricated by using vacuum filtration.

Membranes	Feed Concentration (NaCl, M)	Applied Pressure (bar)	Permeance (L□m ⁻² □h ⁻ ¹ □bar ⁻¹)	Rejection (%)	Reference (#)
NF90 (Dow Filmtec TM)	0.17	5	1.3	50	9
NF270 (Dow Filmtec TM)	0.17	5	8.9	14	9
Modified co – polyamide	0.01	4.5	12.2	63	10
PEI	0.034	5	0.0042	45	11
PEI/N-TNT	0.034	5	0.0074	53	11
PIAM/PS	0.068	10	2.7	10	12
NFC – PVDF – PEI – 1	0.034	7	3.9	65	13
GCTACC/PAN	0.034	12	0.7	57	14
MFI - type zeolite	0.1	20.7	0.0058	77	15

AGO 0.5	0.2	5	36.5	20.45	This Work
GO	0.2	5	6.31	23	This Work
GO TFN	0.034	20.7	2.87	94	20
Base-refluxing reduced GO/PVDF	0.02	5	3.3	40	19
GO ₁₀ coated - PA	0.034	15.5	0.90	96	18
Mesoporous bentonite /α-alumina	0.1	8.2	0.0120	45	17
MFI - type zeolite	0.051	7	0.0142	37	16

Table S1. Comparison of performances of previous nano-filtration membranes with the

 prepared AGO membrane to a NaCl solution

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