

Supplementary Information

Facilitation of Water Penetration through Zero-dimensional Gates on Rolled-up Graphene by Cluster–Chain–Cluster Transformations

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Nanogate size evaluation and size distribution of nanopores

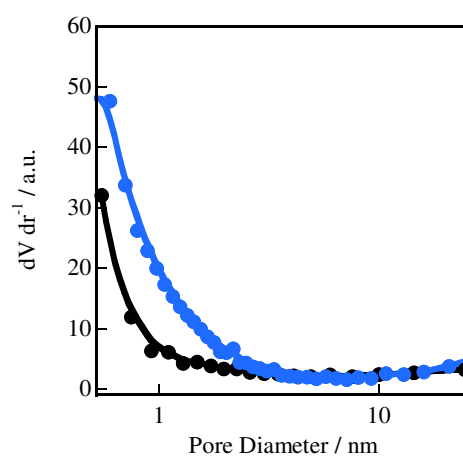


Figure S1. Nanospace size distributions of closed (black curve) and gate (blue curve) NHs, evaluated by Barret–Joyner–Halenda analysis.

Hydrophobicities of samples from X-ray photoelectron and Raman spectroscopy measurements

The surface oxygens of closed, open, and gate NHs were measured by X-ray photoelectron spectroscopy, as shown in Figure S2. Peak analyses showed that the oxygen/carbon (O/C) ratios of closed, open, and gate NHs were 0.03, 0.07, and 0.05, respectively. O/C ratios of typical graphites (Madagascar graphite, acetylene black, and carbon black) were 0.03–0.07, which were used for comparison. These findings demonstrated that closed and gate NHs have hydrophobicities similar to those of graphites. Raman spectra in Figure S3 show that no significant differences were observed for closed, open, and gate NHs. Here the intensity ratios of G/D were 0.95 for a closed NH, 0.94 for an open NH, and 0.95 for a gate NH.

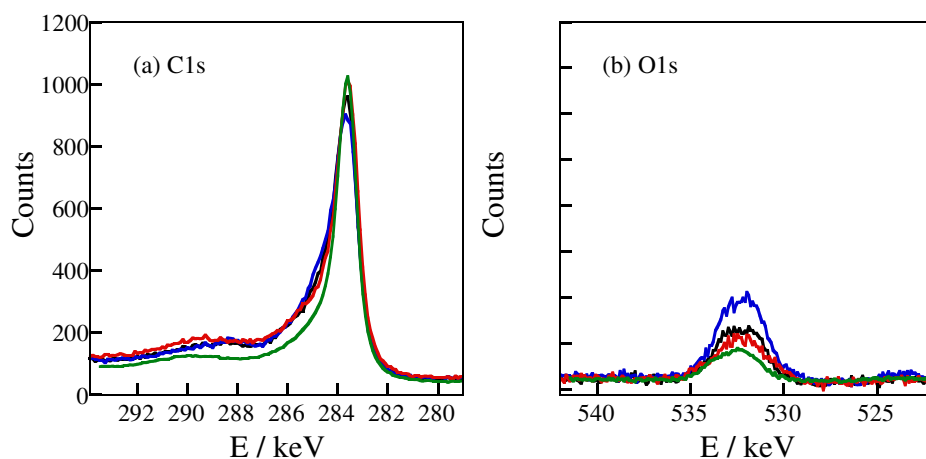


Figure S2. X-ray photoelectron spectroscopy peaks of (a) C1s and (b) O1s for closed NH (black curves), gate NH (red curves), open NH (blue curves), and graphite (green curves).

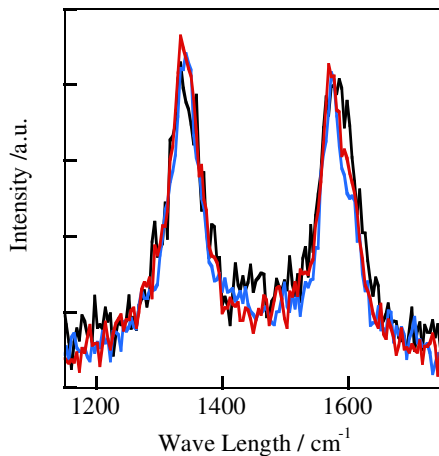


Figure S3. Raman spectroscopy for closed NH (black curves), gate NH (red curves), and open NH (blue curves).

Small-angle X-ray scattering analysis

The Ornstein–Zernike equation is given as follows:

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \quad (\text{S1})$$

Here, ξ and $I(0)$ are the Ornstein–Zernike correlation length and scattering intensity, respectively, at $s = 0$. The density fluctuation is defined as $I(0)/N$ (N : molecular number). The $I(0)$ value can be obtained from the intercept of the Ornstein–Zernike plot, $1/I(s) = 1/I(0) + \xi^2 s^2/I(0)$, as shown in Figure S4. The relative density

fluctuation is $I(0)/I(0)_{\phi=0}$ at $s = 0$ (ϕ : filling factor). The degree of density difference at the boundaries in the models shown in Figure 6 indicates the calculated density fluctuations and is given as follows:

$$RDF_{calc} = \sum_i (\Delta\rho_i)^2 v \quad (\text{S2})$$

Here, $\Delta\rho_i$ is the electron density difference at the boundaries between water, carbon, and void spaces in a pore in the i -th volume element of the model.

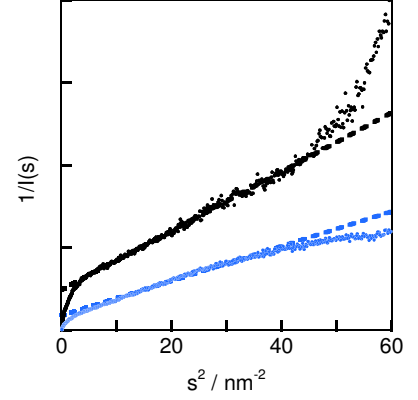


Figure S4. Ornstein–Zernike plots of water-adsorbed closed NH (●) and gate NH (○).

Simulation procedure

Because a water molecule has hydrogen bonds, the intermolecular interactions of water molecules are given by the sum of the dispersion and electrostatic interactions between two hydrogen atoms and two lone pairs, as defined by the TIP5P potential model.

$$\phi_{ff}(r) = 4\epsilon_{ff} \left[\left(\frac{\sigma_{ff}}{r} \right)^{12} - \left(\frac{\sigma_{ff}}{r} \right)^6 \right] + \sum_i^4 \sum_j^4 \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (\text{S3})$$

Here, e_{ff} and s_{ff} are the potential well depth ($e_{ff}/k_B = 80.5$ K) and effective diameter ($s_{ff} = 0.312$ nm), respectively, of water. The absolute values $|q|$ of the charges of the hydrogen atoms and lone pairs are 3.86×10^{-20} C. The distances of the hydrogen atoms and lone pairs from the center of a water molecule are 0.0957 and 0.0700 nm, respectively. The H–O–H and lone-pair–O–lone-pair angles are 104.52° and 109.47° , respectively. The interactions between water molecules and carbon atoms are expressed by the sum of dispersion forces, using the Lennard-Jones potential:

$$\phi_{sf}(r) = 4\epsilon_{sf} \sum_i^s \left[\left(\frac{\sigma_{sf}}{r_{if}} \right)^{12} - \left(\frac{\sigma_{sf}}{r_{if}} \right)^6 \right] \quad (\text{S4})$$

Here, ϵ_{sf} and σ_{sf} are the fitting parameters for the potential depth and effective diameter between a water molecule and carbon atom, respectively ($\epsilon_{sf}/k_B = 49.3$ K, $\sigma_{sf} = 0.327$ nm). These fitting parameters are obtained using the Lorentz–Berthelot rules.

A stable water structure outside the simple NH model at 303 K was determined using a canonical ensemble Monte Carlo (MC) simulation before the molecular dynamics simulation. A random trial of the movement of a water molecule yields a new configuration for the MC simulations. The relationship $\exp(-\Delta E/kT)$, from statistical mechanics, can be used to determine the movement, where ΔE is the

difference between the total energies of the new and current configurations. Molecular dynamics simulations were performed to obtain the dynamics of water penetration through an NH nanogate. The simulations were performed using the general leapfrog procedure with a canonical ensemble. All 400 water molecules moved every 0.1 fs. A temperature range of 303 ± 3 K was maintained using the heat-bath coupling method. The molecular coordinates were output for trajectory analyses. Here, 400 water molecules outside the NH correspond to a filling factor of 0.3. A periodic boundary condition was assigned in a unit cell of size $4 \times 4 \times 6$ nm³. The cutoff length for those potential calculations is 2 nm. The diameter of the NH is defined as the distance between carbon atomic centers, namely 3.26 nm. Subsequently, 2400 carbon atoms were used to construct an NH. A nanogate of diameter 0.4 nm was introduced on the carbon wall of the NH by a deficiency of 21 carbon atoms from the 2400 carbons.