Enhanced Water Evaporation from Å-Scale Graphene Nanopores

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ABSTRACT: Enhancing the kinetics of liquid—vapor transition from nanoscale confinements is an attractive strategy for developing evaporation and separation applications. The ultimate limit of confinement for evaporation is an atom thick interface hosting angstrom-scale nanopores. Herein, using a combined experimental/computational approach, we report highly enhanced water evaporation rates when angstrom sized oxygen-functionalized graphene nanopores are placed at the liquid—vapor interface. The evaporation flux increases for the smaller nanopores with an enhancement up to 35-fold with respect to the bare liquid—vapor interface. Molecular dynamics simulations reveal that oxygen-functionalized nanopores render rapid rotational and translational dynamics to the water molecules due to a reduced and short-lived water hydrogen bonding. The potential of mean force (PMF) reveals that the free energy barrier for water evaporation decreases in the vapor interface. Molecular dynamics simulations reveal that oxygen-functionalized nanopores render rapid rotational and translational dynamics to the water molecules due to a reduced and short-lived water hydrogen bonding. The potential of mean force (PMF) reveals that the free energy barrier for water evaporation decreases in the presence of nanopores at the atomically thin interface, which further explains the enhancement in evaporation flux. These findings can enable the development of energy-efficient technologies relying on water evaporation.

KEYWORDS: graphene nanopores, phase transition, water evaporation, evaporation kinetics, molecular dynamics, enhancement

The unusual effect of nanoscale confinement of water on its properties, including phase transition behavior, is of fundamental scientific interest. Classical explanations such as those based on the Hertz—Knudsen (HK) relationship describing the evaporation of water from bulk surfaces breaks down for water confined in nanoscale pores and channels, and enhanced evaporation fluxes have been predicted. An enhancement in the evaporation flux is attractive for applications such as energy-efficient steam generation, cooling, and desalination technologies for potable water. An enhancement in the evaporation flux with the decreasing dimensions in nanochannels or a single nanopore has been attributed to several effects. These include the formation of an extended meniscus outside the pore entrance, gap-dependent line tension between water and confining container, surface roughness, and surface charge induced concentration change of hydronium ions. The validity of the HK relationship has been questioned while studying liquids in nanoscale confinement where additional complications due to density inhomogeneities and disjoining pressure effects must be considered.

Molecular dynamics (MD) simulations have been widely used to provide molecular insights into evaporation from a bare liquid—vapor interface (BLVI). Due to reduced hydrogen bonds (HBs) at the liquid—vapor interface, water molecules exhibit faster translational and rotational dynamics than the water molecules present in the bulk phase. Yet, only a few studies have focused on the evaporation from nanoscale pores and channels, which are two distinct pore topologies. Enhanced evaporation of water through nanoporous graphene has been attributed to the lowering of the local interfacial free energy and reduced HB networks, while in contrast, modulated capillary and interfacial wetting effects play a role in nanochannels. The ultimate limit of a nanoscale evaporation conduit is a two-dimensional (2D) nanopore with a size commensurate to the water molecule. In this topology, water molecules exiting the nanopore are in contact with only an atomically thick layer of edge atoms. At this limit, the HB networks of water molecules are disrupted, affecting their translational dynamics, which

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in the past has led to interesting phenomena when water is confined at this length scale (e.g., rapid transport of liquid water inside carbon nanotubes).\textsuperscript{2,26,27} The interplay of entropic- and enthalpic-stabilized states of confined water, depending on the extent of hydrogen bonding, has led to the observation of diameter-dependent depression and the elevation in the freezing transition of water leading to the formation of ice nanotubes at unexpectedly high temperatures.\textsuperscript{28} The 2D nanopore, the subject of this communication, is in sharp contrast to other pore topologies realized in recent experiments where exiting water molecules are in contact with extended surfaces depending on the pore geometry.\textsuperscript{29}

Currently, obtaining experimental data on water evaporation from 2D nanopores commensurate with the size of the water molecule is nontrivial. A challenging factor in such a study is to ensure that the evaporation flux is neither controlled by the external mass transfer of the water vapor nor by the rate of supply of the liquid water to the evaporation front.\textsuperscript{29,30} Herein, we address these issues by placing liquid water on a 2D evaporation front composed of single-layer graphene hosting angstrom sized pores. Evaporation was carried out in vacuum in order to diminish the external mass transfer resistance. We observed rapid evaporation from the nanoporous graphene interface with fluxes that were significantly larger than that from the BLVI. The enhancement in the evaporation rate, defined as the ratio of evaporation flux from the graphene nanopores to that from BLVI, increased for the ensemble of nanopores with a smaller pore size, with an enhancement up to 35-fold for the smallest pores. Molecular insights into the enhanced evaporation are obtained with extensive atomistic MD simulations with edge-functionalized nanopores. The presence of nanopores at the liquid–vapor interface increases the translational and rotational dynamics of water molecules in the liquid phase, reduces the number of HBs per molecule next to the interface, and reduces the free energy barrier for water molecules to cross the liquid–vapor interface.

RESULTS AND DISCUSSION

Fabrication and Characterization of Graphene Nanopores. Graphene was synthesized by chemical vapor deposition (CVD) of methane on an annealed Cu foil.\textsuperscript{31} Raman spectroscopy on the as-synthesized graphene confirmed that it was a single-layer film ($I_{2D}/I_G$ ratio of 2.7 ± 0.1; Figure S1). The density of intrinsic defects in graphene was low ($I_{2D}/I_G$ ratio of 0.08 ± 0.03).\textsuperscript{32} Since defect-free graphene is not permeable to water,\textsuperscript{33} we incorporated vacancy defects by exposing as-synthesized films to radiofrequency (RF) O\textsubscript{2} plasma for exposure periods of 1, 2, and 3 s. O\textsubscript{2} plasma generates energetic radicals which graft the graphene lattice with oxygen functional groups eventually leading to pore formation, and in some cases, pore formation is also accelerated by directly knocking out the carbon atoms from
the lattice.\textsuperscript{34} Exposure to O\textsubscript{2} plasma at room temperature for a short time (1 s) is sufficient to incorporate Å-scale vacancy defects (or nanopores) allowing the transport of water molecules as well as light gas molecules.\textsuperscript{35–37} Increasing the exposure time to plasma enlarges the pore size.\textsuperscript{35,36} Therefore, nanopores created by plasma are interesting for studying water evaporation as a function of the nanopore size.

Raman spectroscopy of plasma-treated graphene reveals the presence of significant D (at 1360 cm\textsuperscript{-1}) and G (at 1620 cm\textsuperscript{-1}) peaks, known to be activated in the presence of defects in the graphene lattice (Figure S1). In particular, a low D/G' intensity ratio observed here (<7) is associated with the incorporation of vacancy defects in the graphene lattice,\textsuperscript{38} which is further confirmed by the direct visualization of the porous lattice by aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM, see discussion later). Since nanopores created by oxidative treatment involve oxygen functionalization,\textsuperscript{39–41} the pore edges are expected to be decorated with oxygen-functional groups. However, determining the exact nature of these functional groups has proven to be challenging. Given the importance of the pore edge functional groups in potentially influencing the water transport, we used X-ray photoelectron spectroscopy (XPS) to probe the functional groups in nanoporous graphene. The measurement was carried out after thermally annealing the plasma-treated graphene inside the XPS chamber to desorb the physisorbed ions and contaminants such as hydrocarbons and water. As a control, we also measured XPS data from the as-synthesized graphene without the plasma treatment. As expected, the as-synthesized graphene did not have any oxygen-functional group (Figure S2). In contrast, we could deconvolute the C1s peak in the plasma-treated sample (3 s plasma, Figure 1A) where the positions of the deconvoluted peaks are consistent with the presence of ether/epoxy (C−O, 286 eV) and semiquinone (C=O, 288.3 eV) groups.\textsuperscript{42} Based on the peak intensity, the overall concentration of functional groups was 6.7%. The relative composition of these functional groups can be analyzed by the O 1s peak. However, it was challenging to deconvolute O 1s because of the contribution from copper oxide from the catalytic Cu substrate for CVD, formed by the oxidation of Cu during the plasma treatment. To resolve this, we carried out the plasma treatment on freshly cleaved highly oriented pyrolytic graphite (HOPG) where the atmospheric contaminants were removed by annealing the samples inside the XPS chamber. Deconvolution of the resulting spectra indicates 31% ether, 62% epoxy, and 7% semiquinone (Figure 1B), which renders the overall composition of ether, epoxy, and semiquinone groups on the graphene lattice as 2.1%, 4.2%, and 0.5%, respectively.

Mechanistic studies on the evolution of defects in graphene indicate that semiquinone groups are generated as a result of C−C bond cleavage.\textsuperscript{43,44} Compared with epoxy and ether groups, these groups are exclusively present at the pore edge because of the bonding requirement, and would eventually determine the effective pore size because of their greater steric effects at the pore edge (Figure S4). Based on the density of vacancy defects estimated by AC-HRTEM imaging (ρ\textsubscript{vacancies}) and the concentration of semiquinone groups calculated by XPS (θ\textsubscript{SQ}), one can estimate the number of semiquinone groups per pore, n\textsubscript{SQ}, as follows:

\begin{equation}
\text{n}_{\text{SQ}} = \theta_{\text{SQ}} \times \frac{\rho_{\text{C}}}{\rho_{\text{vacancies}}}
\end{equation}

where ρ\textsubscript{C} is the density of carbon atoms in the graphene lattice. Using eq 1, for the 3 s plasma sample, n\textsubscript{SQ} equals 7, confirming our previous assertion that a pair of semiquinone groups are created on the pore edge by the oxidative cleavage of C−C bond.

AC-HRTEM of graphene films treated with plasma was carried out to understand the density and size distribution of the carbon vacancies. It is extremely challenging to determine the precise structure of functionalized vacancy defects because (i) atmospheric and graphene transfer related contaminants tend to cover the defects, and (ii) electron beam tends to gasify oxygen functional groups. We recently showed that transferring graphene using a lacey carbon film followed by annealing at 900 °C in a reducing atmosphere inside an activated carbon bed is effective in removing the contaminants for imaging vacancy defects in HRTEM.\textsuperscript{45} However, the high-temperature annealing treatment gasifies the oxygen functional groups. As a result, only bare nanopores devoid of functional groups could be visualized (Figure 1C). The removal of the functional groups also tends to coalesce nearby pores. Therefore, we note that pore size and porosity estimated by AC-HRTEM are an overestimate. Therefore, water vapor flux (vapor flow rate normalized to open area in graphene for evaporation where open area is estimated by AC-HRTEM study), and the corresponding enhancement reported in this study are underestimated.

Using AC-HRTEM, we observed increasing porosity in graphene as a function of the plasma time. We then analyzed the gap in the vacancy defects large enough for water transport by an effective pore diameter, d\textsubscript{eff}, as follows (Note S1):

\begin{equation}
d_{\text{eff}} = d_{\text{HRTEM}} - 2b_{\text{C}=\text{O}} - \frac{r_{\text{C,vdw}}}{\sqrt{2}} \tag{2}
\end{equation}

\begin{equation}
d_{\text{HRTEM}} = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4N_{\text{C}}}{\rho_{\text{C}}}} \tag{3}
\end{equation}

where N\textsubscript{C} is the number of missing carbon atoms as determined by AC-HRTEM images (Figure S3B), b\textsubscript{C=O} is the bond length of the semiquinone group (1.2 Å), and r\textsubscript{C,vdw} is the van der Waals radius of carbon.\textsuperscript{46}

We observe nanopores that are both smaller and larger than the size of the water molecule which has a kinetic diameter of 2.65 Å (Figure 1C, Figure S3C).\textsuperscript{47} In this study, we only consider pores that are bigger than water molecules as smaller nanopores are impermeable to water. The distribution of d\textsubscript{eff} is skewed to the right, which is expected when one generates nanopores by oxidative treatment where nucleation and pore expansion are concomitant.\textsuperscript{48} However, a clear trend in d\textsubscript{eff} can be observed; the median d\textsubscript{eff} increases for the longer plasma time (6.0, 6.5, and 6.9 Å for 1, 2, and 3 s, respectively) consistent with the extended pore expansion with the longer plasma time.

**Water Evaporation.** Next, to probe the evaporation of water, the porous graphene film was transferred on a porous W foil hosting an array of 5-μm-sized holes over a mm\textsuperscript{2} area. To prevent cracks and tears in graphene during the transfer and during the transport study, graphene was mechanically reinforced with a 200 nm-thick nanoporous carbon (NPC) film hosting much larger pore opening of 20–30 nm.\textsuperscript{49} We refer to this film as the support film. The W foil supported graphene/support film was subsequently annealed at 500 °C to improve the adhesion of the film with the foil (Figure S5 and
without which the film had the tendency to peel off in the presence of water. The hydrophilic nature of the support film (Figure S7) allowed wetting of the film with liquid water enabling us to successfully conduct the evaporation experiments. For measuring the evaporation flux, the film was sealed inside a stainless steel module, and liquid water was loaded on the side of the support film at ambient conditions (Figure 2A). The temperature of the liquid side was monitored by a thermocouple placed near the graphene film and was found at 22 °C. The other side (vapor side) of the film was connected to a vapor collection chamber with volume $V$, maintained at a low pressure (0.5−0.6 Torr) with a vacuum pump. To initiate the measurement of water vapor evaporation rate, the collection chamber was isolated from the vacuum pump at a set time which allowed accumulation of water vapor in the collection chamber, witnessed by rise in the chamber pressure.

Figure 2. Water evaporation data from graphene nanopore compared to that from BLVI and the support film. (A) A schematic of the water permeation setup and water permeation through the support film, nanoporous graphene, and eventually in a vacuum. (B) The raw data of water permeation tests from nanoporous graphene films. The $R^2$ values of each linear regression are 0.996, 0.99, and 0.992, for median $d_{eff}$ of 6.0, 6.5, and 6.9 Å, respectively. (C) Five evaporation measurements on the same graphene film, PG-1. (D) Water flux from nanopores of each film, and their comparison with BLVI and the support film, NPC (20−30 nm-sized pore opening) at the bulk liquid temperature of 22 °C. From left to right, the columns denote PG-1 to PG-8. (E) Comparison of evaporation enhancement between each nanoporous graphene film. The enhancement factor is defined as the ratio of water flux from the nanopores of a graphene film to the water flux from the BLVI. Error bars in (D) and (E) represent the standard deviation of three (BLVI) or five repeated measurements (graphene and support film).
The measurement of the water evaporation rate by the above protocol allowed us to study evaporation in a regime where the external mass transfer of water vapor is not the rate-limiting step. On the liquid water side, the supply of water to the graphene interface was orders of magnitude higher than the limiting step. On the liquid water side, the supply of water to the evaporation front was also not the rate-limiting step. It is reported that the heat transfer limitation in evaporation becomes negligible compared with the interfacial evaporation kinetics when using a material with a thermal conductivity, $k$, much larger than that of the working liquid. Therefore, the use of a stainless steel module in this study ensures that the evaporation is not limited by heat transfer from the surroundings because of an order of magnitude higher thermal conductivity of stainless steel compared with water. We used the same stainless steel module for BLVI, support film, and the graphene film with only one exception that graphene and the support film had an area of 1 mm$^2$, whereas the area of BLVI was 133 mm$^2$ to ensure a reliable measurement (Figure 2A and S9; see details in Methods).

We prepared 2–3 porous graphene films for each plasma condition (a total of 8 films, referred to as PG-1 to PG-8). Before water evaporation tests, we ensured the integrity of the films by pressurizing them with H$_2$ and measuring the gas transport. Only films which showed no signs of tears or cracks, marked by orders of magnitude lower gas flow rate from porous graphene compared to the support film, were used for the water evaporation study. A comparison of the gas transport data on a specimen before and after the water evaporation test revealed that there were no significant differences in the gas transport properties (Figure S13B), confirming that the nanopores did not expand during the evaporation study.

This was also supported by the O 1s XPS spectrum, showing that the composition of oxygen-functional groups did not change after exposure to water in a typical water evaporation condition (Figure S13A).

Before each water evaporation experiment, a leak test was performed by isolating the collection chamber from the vacuum pump and the module containing nanoporous graphene. We did not witness any significant increase in the pressure of the collection chamber during this test, indicating negligible leak into the chamber from the atmosphere (Figure 2B). In contrast, when the graphene module was not isolated while the vacuum pump was isolated, the pressure in the chamber rose sharply with a near constant rate with respect to time. The near constant rate in these measurements is driven by the fact that the driving force for evaporation, the difference between the saturation vapor pressure of water (24 Torr) and the vapor pressure in the chamber (0.5–2 Torr), does not change significantly.

We obtained effective evaporation flux from BLVI of 0.69 ± 0.04 mol m$^{-2}$ s$^{-1}$ at the bulk liquid temperature of 22 °C (Figure S11). This flux is consistent with BLVI flux data reported in the literature using reservoirs made up of stainless steel containers and using evaporation to induce evaporation (Table S1). Additionally, the flux from the bare support film (0.59 ± 0.14 mol m$^{-2}$ s$^{-1}$) was close to that of BLVI, indicating that 20 nm pores of the support film do not yield enhancement. This contradicts the literature on enhancement from a similar-sized single nanopore. This is attributed to the lack of an extended meniscus in our millimeter-scale liquid–vapor interface created by the support film in contrast to the literature where a single nanopore with finite depths creates the presence of an extended meniscus.

To understand the effective evaporation enhancement contributed by the graphene nanopore at the liquid–vapor interface, we used eqs 5 and 6 to estimate water flux and compared it to the corresponding value from the BLVI (Figure 2D).

\[
\text{water flux from nanopores} = \frac{\text{evaporation rate (mol/s)}}{\text{pore area, } A_{\text{tot}}} \quad (5)
\]

\[
A_{\text{tot}} = \sum_{d_{\text{eff}}>d_{\text{water}}} \rho f d_{\text{eff}}^2 \quad (6)
\]

The total pore area, $A_{\text{tot}}$, was estimated by using the pore size distribution of $d_{\text{eff}}$ (Figure S3C), the relative frequency, $f$, of each observed pore, and the pore density, $\rho$, estimated by the AC-HRTEM study. We only consider pores whose $d_{\text{eff}}$ is larger than the kinetic diameter of water, $d_{\text{water}}$ (∼0.26 nm). The calculated porosities were 0.42%, 0.44%, and 1.30% for samples with median $d_{\text{eff}}$ of 6.0 Å, 6.5 Å, and 6.9 Å, respectively. Compared with the measurement of evaporation flux from the BLVI, we found that the evaporation fluxes from graphene nanopores were largely enhanced (Figure 2D). The water evaporation fluxes from two separate nanoporous graphene samples (PG-1 and PG-2) with median $d_{\text{eff}}$ of 6.0 Å were 24 ± 3 and 12 ± 2 mol m$^{-2}$ s$^{-1}$ (Figure 2D), corresponding to enhancements of 35 ± 4 and 17 ± 3, respectively (Figure 2E). The fluxes of the other set of nanoporous graphene samples (PG-3, PG-4, PG-5) with a slightly larger median $d_{\text{eff}}$ of 6.5 Å was comparatively lower (8.9 ± 0.4, 8 ± 0.5, and 6 ± 0.9 mol m$^{-2}$ s$^{-1}$, Figure 2D), corresponding to enhancements of 13 ± 0.6, 12 ± 0.7 and 9.1 ± 1.4, respectively (Figure 2E). The fluxes from the samples (PG-6, PG-7, PG-8) with the largest median $d_{\text{eff}}$ (6.9 Å) was the lowest (2.4 ± 0.4, 2 ± 0.4, and 0.94 ± 0.18 mol m$^{-2}$ s$^{-1}$, Figure 2D), corresponding to enhancements of 3.5 ± 0.6, 2.8 ± 0.6, and 1.3 ± 0.25, respectively (Figure 2E). We note that in AC-HRTEM, the electron beam tends to gasify oxygen functional groups and thereby coalesce nearby pores, leading to overestimated pore size and porosity. Therefore, here the evaporation enhancement may be underestimated. Overall, we observed enhanced water evaporation fluxes for all nanoporous graphene samples considered in this study, with enhancement...
increasing for smaller nanopores. We finally point out that although it is customary to use the Hertz–Knudsen and its variants to characterize evaporation, we refrain from using this formulation due to the underlying equilibrium framework used while deriving the Hertz–Knudsen relation.

While the water evaporation rate decreased for increasing pore size, the H$_2$ transport rate showed a reverse trend (i.e., it increased for the larger pores; Figure 3). The latter is consistent with the gas transport mechanism (i.e., hydrogen flow is proportional to the pore area; eq 7).

$$j_{H_2} = \frac{A_p \Delta P}{\sqrt{2 \pi m k_B T}}$$  \hspace{1cm} (7)

where $P$ is the feed pressure, $m$ is the mass of H$_2$, $A_p$ is the area of the pore, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

The increased water evaporation fluxes from the ensemble of nanopores with the smallest median $d_{\text{eff}}$ indicate a strong role of nanopore edge driven confinement effects on interfacial water that controls the evaporation flux. Next, to understand the observed enhancement, we carried out MD simulations on water evaporating from graphene nanopores.

**System Details for Molecular Dynamics Simulations.** We simulated four different sized nanopores by removing 16, 22, 52, and 94 carbon atoms from the pristine graphene, which are referred to as type-0, -1, -2, and -3 nanopores, respectively. The carbon atoms on the nanopore edges were terminated with hydrogen atoms (H), ether (ET), and hydroxyl (OH) (Figure 4A–C and Figure S14) to study the effect of pore-edge functional groups on the water evaporation flux. Density functional theory (DFT) calculations revealed that the nanopore edges alternately terminated with H atoms, and the oxygen-functional groups had the lowest formation energies (Note S6, Figure S15, S16).

$d_{\text{eff}}$, based on the diameter of the largest van der Waals sphere that can be accommodated in the functionalized nanopore, are listed in Table S3. This method reliably captures the effective pore area consistent with the gas transport mechanism (i.e., hydrogen flow is proportional to the pore area; eq 7).

$$j_{H_2} = \frac{A_p \Delta P}{\sqrt{2 \pi m k_B T}}$$  \hspace{1cm} (7)

Panels (F) and (G) are the side and top view of the cylindrical volume considered for analyzing water properties. (H) Density profile of water molecules in contact with the FNPG located at $z = 0$ (black dashed line). $z > 0$ and $z < 0$ represent liquid and vapor regions, respectively. The location of the first hydration layer of thickness $\sim 0.5$ nm is also illustrated (black dotted line).
Evaporation Flux of Water Molecules. The water evaporation flux, $j$ (molecules nm$^{-2}$ ns$^{-1}$) (Figure 4E) at 25 °C was evaluated from the slopes of the net number of water molecules exiting the nanopores (Note S9, Figure S21). In the absence of FNPG, the evaporation flux from a BLVI interface was 0.081 molecules nm$^{-2}$ ns$^{-1}$, in good agreement with the value of $\sim$0.085 molecules nm$^{-2}$ ns$^{-1}$ predicted by Julin et al.$^{60}$ for the TIP4P-Ew water model at 27 °C. In the presence of FNPG, the water evaporation flux increased monotonically with decreasing $d_{\text{eff}}$ (Figure 4E), irrespective of the nanopore functionality, consistent with our experimental findings. Interestingly, the presence of oxygen functional groups enhanced the evaporation flux. The greatest enhancement with respect to BLVI was $\sim$13.3-fold, observed for the smallest OH-terminated nanopores (OH$^{-}$) with a flux of 1.081 ± 0.002 molecules nm$^{-2}$ ns$^{-1}$ (Table S4). For the largest nanopores, the flux approaches the BLVI flux. The observed enhancement factors in the simulations are in the same order of magnitude as those observed experimentally.

Figure 5. HB analysis for the functional group (pore)–water (P–W) pair and water–water (W–W) pair along with rotational dynamics and translational dynamics of water molecules present in the ROI of different FNPGs. Panels (A), (B) and (C) show type-1 nanopores terminated with H atoms, ET and H, and OH and H respectively. Water molecules (green) in the vicinity of the nanopores are shown along with the HBs (black dotted lines) between different pairs. (D) Average number of HBs per water molecule formed between functional groups terminating the nanopores and water molecules present in the ROI. The same for the water molecules present in the “10–90” interface of BLVI is shown for comparison. (F) Lifetime of HBs formed between functional groups terminating the nanopores and water molecules present in the ROI. (G) Lifetime of HBs formed between the water molecules present in the ROI. Lifetime of HBs formed between water molecules present in the “10–90” interface of BLVI is shown for comparison. (H) Dipole relaxation times of water molecules present in the ROI for $l = 1$. Dipole relaxation times of water molecules present in the “10–90” interface of BLVI is shown for comparison. (I) MSD of water molecules in z direction present in the ROI of FNPGs with type-1 nanopores. MSD of the water molecules in z direction, present in the “10–90” interface of BLVI is shown for comparison. Due to insufficient sampling in the ROI of type-0 nanopores, we report the values for type-1, -2 and -3 nanopores only. The standard error in mean of the reported values in panels D–H is very small and hence are not seen easily.

(A$_{\text{eff}}$ Table S3) available for evaporation from the pore topologies we have used in this study. All atom MD simulations to study the evaporation through the functionalized nanoporous graphene (FNPGs) were carried out with a TIP4P-Ew water bath, and an attractive pristine graphene surface (attractive wall) placed 8 nm away from the FNPG (Note S8, Figure S17) is used to capture evaporated water molecules (Figure 4D).
of magnitude as those observed in the experiments (Figure 2E). In experiments, while ether and semiquinone functional groups (C=O) are present substantially at the pore edge, epoxy functional groups are found to be barely present at the pore edge. Therefore, in addition to the functionalized nanopore flux data reported here, we also carried out simulations with edges functionalized with semiquinone functional groups for $d_{ed}=0.345$ nm ($j=0.844 \pm 0.003$ molecules/nm$^2$) and $0.461$ nm ($j=0.701 \pm 0.002$ molecules/nm$^2$) and found that the fluxes were between the values obtained for the OH and ether groups.

In order to explain this increase in the water evaporation flux, we focused our attention on the properties of water molecules present in the cylindrical volume adjacent to the nanopore, as shown in Figure 4F,G. The length, $l$, of this cylindrical volume is equal to the thickness of the first hydration layer of FNPG (Figure 4H), and its diameter is equal to $d_{ed}$. We refer to these cylindrical regions as the region of interest (ROI) in the forthcoming sections. For BLVI, we focused our attention on properties of water molecules present in the “10–90” interface ($\text{Note S9, Figure S20}$).

**Hydrogen Bond Analysis, Rotational Dynamics, and Translational Dynamics.** For the water molecules present in the ROI, HBs formed with the edge functional groups$^{59,60}$ and HBs formed between water molecules$^{62}$ were analyzed using a geometric criterion. Since OH functional groups can act as both HB donors and acceptors, their propensity to form HBs with water is greater when compared with the ET functional groups that can act only as HB acceptors (Figure 5B–D). For the H-terminated nanopores, the carbon atoms to which these H atoms are bonded are not sufficiently electronegative ($\text{Note S16}$) to form HBs with water and we did not observe any HBs in this situation (Figure 5A). Nevertheless, the H-terminated FNPGs assist in breaking water–water HBs, albeit at a lesser extent via the asymmetry imposed upon the water molecule by the FNPG surface.$^{63}$

This enhancement of HBs with functional groups results in the greatest reduction in water–water HBs in the ROI of FNPGs terminated with OH functional groups (Figure 5E). We point out that the water molecules in the ROI for all FNPGs displayed a reduced number of HBs when compared with water molecules present in “10–90” interface (2.75 ± 0.002). The presence of functional groups disrupts interactions between water molecules present in the ROI by breaking HBs between them (Figure 5E and Table S5), allowing for a greater escape tendency through the nanopores. This trend correlates with the highest evaporation flux observed for OH-functionalized nanopores (Figure 4E), consistent with the increased disruption of HBs with decreasing nanopore size ($\text{Note S10}$). For the smallest nanopore (type-0), water molecules in ROI interact mainly with the functional groups (Figure S22). A qualitatively similar increase in the evaporation flux has been observed by adding charges to the edge carbon atoms to mimic the presence of functional groups.$^{59}$

In addition to the number of HBs, the HB dynamics of water molecules in the ROI provides additional insight into the enhanced evaporation flux with decreasing nanopore size. From the intermittent HB correlation function, $C_{HB}(t)$,$^{64,65}$ we obtained HB lifetime, $\tau_{HB}$, using a single exponential fit ($\text{Note S11}$). As compared to the water molecules present in the “10–90” interface of BLVI, water molecules present in the ROI of FNPGs show reduced number and reduced lifetime of HBs (Figure 5E,G and Table S5). Lower $\tau_{HB}$ values revealed faster dynamics for HBs for the OH-terminated FNPGs when compared with the ET-terminated FNPGs. This trend was observed for functional group-water (Figure 5F) as well as water–water HBs (Figure 5G). The reduced $\tau_{HB}$ for the OH groups is partly due to the increased steric effects at the pore edge when compared with the ET groups (Figure 5B, C). Additionally, the lower $\tau_{HB}$ for the water–water HBs (Figure 5G) correlates directly with the decreased water–water HBs in the ROI (Figure 5E). For a given pore functionality, the $\tau_{HB}$ values between water present in the ROI and the functional groups are relatively invariant with $d_{ed}$ (Figure 5F). The observed $\tau_{HB}$ values are specific to the given functional group and water pair. The reduction in $\tau_{HB}$ is the greatest for FNPGs terminated with OH functional groups which effectively reduces the HB lifetimes. We point out that both the number of HBs and $\tau_{HB}$ play an important role in the escape probability of the water molecule. Smaller $\tau_{HB}$ indicates shorter lived HBs, resulting in faster HB dynamics to render enhanced evaporation fluxes (Figure 4E).

As another measure of the altered water dynamics and relaxation, we evaluated the dipole–dipole reorientational dynamics by computing the first, $\langle l = 1 \rangle$ and second rank ($\langle l = 2 \rangle$) Legendre polynomials of the water dipole moment in the ROI as well as the corresponding dipole relaxation times, $\tau_2^l$ ($\text{Note S12}$). $\tau_2^l$ values for water molecules present in the ROI of different FNPGs are smaller than the $\tau_2^l$ values of water molecules present in the “10–90” interface of BLVI ($\tau_2^l = 4.67$ ps and $\tau_2^l = 1.70$ ps) (Figure 5H). For a given pore diameter, the dipole relaxation times were lowest for the OH-functionalized pores and highest for the H-terminated pores (Figure 5H and Tables S6, S7), reflecting the trends in the HB lifetimes (Figure 5G). Additionally, faster HB and dipole–dipole reorientational dynamics were observed at the smaller nanopore sizes because of their tendency to effectively disrupt the interaction between water molecules in the ROI (Figure S22). The local water dynamics are dependent on the ability of the water molecule to both form and break HBs at a given instant.$^{66,67}$ Our results clearly reveal the presence of faster HB and dipole–dipole reorientational dynamics for water in the ROI of the nanopores accentuated by edge functionalization with the greatest reduction in relaxation times observed for the OH-functionalized nanopores. The trends in these dynamic quantities are consistent with the enhanced evaporation flux with decreasing $d_{ed}$ observed in experiments, where the increased presence of oxygen as either ET or epoxy and semiquinone at the nanopore edge was found to correlate positively with enhanced evaporation.

A direct dynamic measure of the propensity of a water molecule to exit the liquid–vapor interface can also be obtained from the variation of the mean square displacement (MSD) of water molecules along the $z$-axis of the ROI, illustrated for the FNPGs with type-1 nanopores in Figure 5I (Figure S25 for other pores). Due to the limited spatial extent sampled in the $z$-direction, we did not attempt to extract a diffusion coefficient. However, the data clearly revealed the increased MSD, for all nanopores relative to the MSD, of water molecules present in the “10–90” interface of BLVI (Figure 5I and Note S13). Despite the limited extent of the distance sampled in the $z$-direction, the MSD plots for the water molecules present in the ROI for different FNPGs showed a distinct transition from the ballistic regime (where MSD scales as $t^2$) at short times to the diffusive regime (where MSD scales as $t$) at longer times. The relative increase in the...
MSD with respect to water molecules present in the “10–90” interface of BLVI diminishes with increasing $d_{\text{eff}}$ as expected (Figure S22 and S25).

**Potential of Mean Force and Surface Tension Analysis.** The variation of the potential of mean force (PMF) for a water molecule along the z-axis of the ROI for different FNPGs are illustrated in Figure 6A,B for the smallest (type-0) and largest (type-3) nanopores, respectively (Figure S26 for other nanopores). A clear decrease in the free energy barrier for moving a water molecule from the bulk liquid (denoted as “$i$” in Figure 6A) to the vapor phase (denoted as “$v$” in Figure 6A) in the immediate vicinity ($-1.5 \text{ nm} < z < 0$) of the FNPG when compared with the PMF for BLVI is observed (Figure 6A,B). The PMF values in the bulk vapor phase (denoted as “$bv$” in Figure 6A) are similar for the different systems reflecting the constant free energy difference for transferring a water molecule between the bulk liquid and the bulk vapor phases. From the PMF variations, we obtained the change in Gibbs free energy ($\Delta G = G_v - G_l$) for transferring a water molecule from the liquid phase (“$l$”) to the vapor region (“$v$”). In all the FNPG systems, we observed a reduction in $\Delta G$ when compared with the value of $\Delta G = 29.87 \text{ kJ/mol}$ obtained for evaporation from a BLVI (Figure 6C). We saw the lowest $\Delta G$ values for type-0 nanopores with the smallest $\Delta G = 22.13 \text{ kJ/mol}$ for OH–0 nanopores (Table S8). The free-energy difference decreases with increasing $d_{\text{eff}}$ primarily due to the ineffectiveness of larger pores in disrupting water–water HBs (Figure S22). However, even for the largest nanopore studied, $\Delta G$ values were slightly smaller than the BLVI values, approaching the BLVI values for the largest H-terminated pores (Figure 6C). The variations in $\Delta G$ (Figure 6C) are consistent with the enhanced evaporation observed for the OH–, ET–, and H-terminated nanopores (Figure 4E).

Due to the enhanced density in the contact water layer formed adjacent to the FNPG, a distinct global minimum (denoted as “$m$” in Figure 6A) in the free energy profile was observed at $z = 0.35 \text{ nm}$ coinciding with the minima in the density distribution (Figure 4H) where the water molecule resides prior to escaping into the vapor phase. Since an evaporating water molecule located at the minimum has to overcome a free energy barrier across the FNPG to enter the vapor phase, we also evaluated the free energy barrier for a water molecule to translocate ($\Delta G_i = G_i - G_m$) from this minimum to the interface (denoted as “$i$” in Figure 6A). In all cases, $\Delta G_i$ values were smaller than the corresponding $\Delta G$ values larger than 16.40 kJ/mol obtained for the BLVI, indicating the lowered barrier for evaporation due to the presence of the nanopores (Table S8). For the OH–0 nanopores, a significant reduction was observed, with $\Delta G_i = 6.57 \text{ kJ/mol}$. Interestingly, only a marginal increase was observed for the free energy change ($\Delta G = G_i - G_l$) between the vapor region (“$v$”) and the interface (“$i$”) across the different pore types lying between 17.28 kJ/mol for OH–0 nanopores and 18.87 kJ/mol for H–3 nanopores. Further, this free energy change was slightly higher than 16.40 kJ/mol obtained for the BLVI (Table S8). These differences are, however, less than $1 k_B T$ (2.49 kJ/mol) at 298...
K (25 °C), indicating that the enhancement in evaporation flux is governed mainly by the larger differences in $\Delta G$, driven primarily by the interaction between functional groups and water molecules in the ROI (Figure S22).

Since we observed an increased evaporation flux from both experiments and MD simulations for the nanopores, we computed interfacial tension ($\gamma$) at the water–vapor interface using the Kirkwood pressure tensor formulation [6, 68] (Note S15). Unlike the BLVI, in the case of the nanopores, the pressure tensor computation was carried out in the ROI. Figure 6D illustrates the surface tension at the water–vapor interface for different FNPG systems. The greatest decrease in $\gamma$ was observed for the type-1 nanopores, and the smallest value of 59.0 ± 0.02 mN/m was observed for the OH–I nanopores correlating with the highest flux observed in the MD simulations (Figure 4E). Additionally, for a given pore type, the greatest reduction in $\gamma$ occurred for the OH-functionalization followed by the ET-functionalization with the least reduction observed for the H-terminated nanopores (Figure 6D and Table S9). This is consistent with the greatest reduction in hydrogen bonding patterns observed for the OH-terminated nanopores which results in the decreased differences between the normal and tangential pressure components at the nanopore interface (Figure S27).

We note that previous studies attributed the enhanced evaporation to the extended meniscus or evaporation area [28, 69] outside the hydrophilic mouth of the nanopores or nanochannels. In our case, the support film hosting 20 nm-sized pore opening was a film with macroscopic length-scale (1 mm$^2$); therefore, it did not have any significant extended meniscus, and we did not observe any enhancement from the support film in control experiments. For nanoporous graphene, one can rule out the existence of an extended liquid film on the vapor side of the graphene film as the basal plane of graphene is inherently hydrophobic. This is also evidenced by the imaging of nanopores obtained by oxidative treatment where oxygen-functional groups are clustered around the pores leaving a pristine hydrophobic basal plane between the pores. [30] In addition, this has also been recently borne out in molecular simulations of water adsorption on graphene oxide surfaces. [30] Therefore, the observed enhancement could be explained by the hydrogen bonding dynamics in a confined geometry of graphene nanopores, as shown by the MD simulation.

CONCLUSIONS

We report a significant enhancement in water evaporation flux, up to 35-fold compared with BLVI, when millimeter scale 2D graphene film hosting billions of oxygen-functionalized Å-scale pores is positioned at the liquid–vapor interface, with enhancement exhibiting a strong dependence on the pore size. We discuss that enhancement from porous graphene in our study is obtained without any extended liquid meniscus and is linked to the rapid hydrogen bonding and orientational dynamics of water in the vicinity of the nanopore rendered by the strong interaction between the water molecule and the pore edge oxygen-functional groups. This results in a decreased free energy barrier for water crossover to the vapor phase, thereby leading to an enhanced evaporation flux. Enhancement increases for the smaller pores because water molecules have a higher probability to interact with the edge functional groups in smaller pores.

The state-of-the-art studies on evaporation of water confined in nanopores were mainly limited to the solid state pores that were several nanometers in size and length. Therefore, this study constitutes the ultimate limit for the confinement of the liquid/vapor interface where the interface is only atom thick, and pores are commensurate to the size of water molecules. This was possible by carefully placing crack-free nanoporous graphene film on the water–vapor interface while ensuring that the liquid supply to the interface as well as the mass transfer of vapor away from the interface were not the rate-limiting step. Opposite flux trends observed for water evaporation rate and gas transport as a function of pore size from the same film adds robustness to our conclusion.

Overall, this study provides an experimental demonstration of significantly enhanced water evaporation flux from a 2D nanoporous interface hosting Å-scale pores. The enhancements observed here can be attractive for applications dependent on the phase change of liquid water. The findings in this study are expected to aid the development of evaporation-based separations (e.g., membrane distillation).

METHODS

Synthesis of Single-Layer Graphene by Low-Pressure Chemical Vapor Deposition (LPCVD). Single-layer graphene was synthesized by the LPCVD process using a preannealed copper foil (50 μm thick, 99.9% purity, Stream). Briefly, the foil was subjected to CO$_2$ and H$_2$ atmosphere at 1000 °C for 30 min, respectively. Subsequently, 24 sccm of CH$_4$ and 8 sccm of H$_2$ were introduced into the reactor at a total pressure of 460 mTorr for 30 min. The reactor was then rapidly cooled down to room temperature once the synthesis was done.

Generation of Pores in Graphene Using O$_2$ Plasma. Incorporating nanopores in the graphene lattice was done by radiofrequency powered O$_2$ plasma. Briefly, the as-synthesized graphene on a copper foil was placed in the chamber of a plasma generator (MTI, EQ-PCE-3, 13.56 MHz, 18 W). Afterward, the chamber was first evacuated and then maintained at total pressure of 80 mTorr under a continuous O$_2$ flow. Following this, plasma was initiated for 1–3 s to generate nanopores.

Fabrication of Porous Support Film on Graphene. The fabrication of porous support film on graphene was carried out following a method reported before. [30] Briefly, the precursor of NPC was prepared by dissolving 0.1 g of poly(styrene-$\beta$-4-vinylpyridine) and 0.2 g of turanose in 2 g of N,N-dimethylformamide. Subsequently, the solution was heated at 180 °C for 3 h. The NPC film was obtained by spin coating the solution on porous graphene resting on a Cu foil followed by pyrolysis at 500 °C in a H$_2$/Ar atmosphere for 1 h. The resulting graphene film, now supported by NPC film, was then placed in a Na$_2$S$_2$O$_3$ bath to remove the Cu foil. After that, the floating graphene/NPC film was rinsed in deionized water several times and then was transferred onto a macroporous tungsten foil hosting an array of 5 μm pores.

AC-HRTEM Imaging. The samples for AC-HRTEM were prepared by transferring porous graphene to 400 mesh Au TEM grids using a porous polymer-assisted transfer method reported elsewhere. [35] Briefly, a thin porous polybenzimidazole copolymer (fumion AM provided by FUMATECH BWT GmbH, Germany) film was first prepared on top of a Cu foil by the nonsolvent-induced phase separation. This film acts as a lacey support for the transfer of graphene from Cu to the TEM grid. The polymer film was then wet-transferred on the porous graphene sample and pyrolyzed at 500 °C in the flow of H$_2$/Ar leading to reinforcement of porous graphene with lacey carbon film. The Cu foil below the graphene film was then etched in an etchant bath, and the resulting reinforced graphene film floating on water was transferred to the TEM grid. Before imaging, the reinforced nanoporous graphene samples were cleaned inside
activated carbon at 900 °C for 1 h in the presence of H₂ to remove contaminations covering the nanopores.

AC-HRTEM was performed using a double-corrected Titan Themis 60–300 (FEI) equipped with a Wein-type monochromator. An 80 keV incident electron beam was used for all experiments to reduce the electron radiation damage. The incident electron beam was monochromated (“rainbow” mode illumination) to reduce the effects of chromatic aberration, and a negative Cs of ~17–21 μm with slight overfocus were used to give a “bright atom” contrast in the images. In addition, a slit was used to expose only the area of the sample being imaged to the electron beam. The images were processed using average and bandpass filters.

**Other Characterization.** Scanning electron microscope (SEM) images were obtained by using FEI Teneo scanning electron microscope at 1.0–5.0 kV and working distances of 2.5–5.0 nm. No conductive coating was applied to the substrates before SEM. TEM imaging and selected area electron diffraction (SAED) of the composite graphene film were conducted by FEI Tecnai G2 Spirit TWIN transmission electron microscope with a 120 kV incident electron beam. Raman measurement was carried on graphene on a Cu foil right after the synthesis and pore etching using 457 nm excitation and Renishaw micro-Raman spectroscopy with 100× objective. The obtained Raman data was analyzed using a MATLAB script. For the calculation of the D and G peak heights, the background was subtracted from the Raman data using the least-squares curve fitting tool (Isqnonlin). X-ray photoelectron spectroscopy (XPS) measurements on O₂ plasma-treated N-SLG resting on a Cu foil were carried out on Axis Supra (Kratos Analytical) using the monochromated Kr X-ray line of an aluminum anode. The pass energy was set to 20 eV, and the step size was set to 0.1 eV. The peak fitting was performed using CasaXPS, and Shirley method was used for background subtraction.

**Hydrogen Transport.** The measurement of hydrogen transport through porous graphene was carried out in a homemade permeation cell (Figure S8). The mass flow controllers (MKS) were precalibrated using a bubble flow meter, delivering a predetermined amount of H₂ to the feed side. The permeate side was swept with Ar at 1 bar. The permeate was connected to a precalibrated mass spectrometer allowing real-time analysis of the permeation rate. The absolute pressure difference between the feed and the permeate sides was kept at 1–1.5 bar. The nanoporous graphene on a tungsten support was sealed in a VCR-based module using two metal gaskets. The gas flow was calculated once the steady state was reached. The permeance, P, of the gas was calculated according to eq 8.

$$J_{H_2} = \frac{X}{AD\Delta P} \quad (8)$$

where X is the flow rate of H₂, A is the area of the nanoporous graphene film, and ΔP is the pressure difference between the feed and the permeate sides for H₂.

**Water Evaporation Measurements.** Water evaporation experiments were performed using a constant volume/variable pressure test method similar to the literature. Briefly, nanoporous graphene on tungsten supports were sealed in a VCR-based module using two metal gaskets (Figure S9A,B). The feed side (support film side) was filled with liquid water (Milli-Q water). The permeate side had a constant volume chamber which was evacuated to 500–600 mTorr using a scroll pump (Figure 2A). The measurement was initiated once the valve connected to the pump was closed isolating the permeate side from the vacuum pump and the valve connected to VCR module hosting nanoporous graphene was opened allowing the collection of water vapor in the constant volume chamber. The corresponding pressure rise in the constant volume chamber was then measured using a pressure transducer (Omega engineering, PX409-USBH). The entire setup was carefully sealed to ensure a leak-free operation. The water evaporation flux was calculated using the ideal gas equation. The volume of the chamber was 5.9 mL in the measurement of graphene film and the support films.

The evaporation flux from the BLVI was measured using the same setup and evaporation conditions with one modification. In this case, a perforated W foil without membrane on top was placed in the VCR module filled with Milli-Q water (Figure S9C). The volume of the chamber was 184 mL in the measurement of BLVI.

**DFT Calculations.** Quantum ESPRESSO was used to carry out DFT calculations to investigate the optimal structure of functionalized graphene nanopore. The plane-wave basis sets were used. Cutoffs of 50 and 500 Ry were employed for the wave function and charge density, respectively, for the electronic wave function expansion. Perdew–Brake–Ernzerhof functional was used to describe the exchange-correlation. Ultrasoft pseudopotentials were employed for the interactions between the ionic core and valence electrons. A vacuum of 2 nm was used to avoid interactions between the periodic images along the direction normal to the FNPGs surface.

Due to the large supercell, the Brillouin zone sampling was restricted to the Γ point. Broyden–Fletcher–Goldfarb–Shanno scheme was employed to perform structural relaxation until the Hellmann–Feynman forces were less than 0.001 Ry/bohr. London dispersion corrections were described using DFT-D2 functional. The relaxed unit cells were replicated in x-y plane to generate FNPGs with four functionalized nanopores.

**Charge Calculations.** Partial atomic charges of the relaxed FNPGs employed in the molecular topology used for MD simulations were obtained using charge calculations based on the CHELPG scheme at the level of the Hartree–Fock/6-31G* basis set using Gaussian09 software. The partial atomic charges on the functional groups and the carbon atoms to which these functional groups are attached are given in Note S16. The partial atomic charges on the complete unit cell of the FNPGs employed in the molecular topology used for the MD simulations are available upon request. Using this method for charge determination, the partial atomic charges on the functional groups are in good agreement with the OPLSAA charges as well as charges used in other functionalized graphene and nanopore simulations with water.

**MD Simulations.** All MD simulations were performed using GROMACS 5.1.4 simulation package. For all cases, the attractive wall, the FNPG, and the piston were located perpendicular to the z-axis. Owing to the hexagonal lattice of graphene, a parallelepiped simulation box was used.

For water evaporation simulations through FNPGs, a water box with 8290 water molecules was equilibrated at 25 °C (298 K) and pressure of 1 bar. The dimensions of the water box after equilibration were a = 4.6046 nm, b = 4.6046 nm and c = 7 nm. This water box was subsequently enclosed along the z axis with the FNPG and a piston to create the water reservoir for evaporation studies. An attractive wall was placed at a distance of 8 nm from the FNPG in the vapor space. A vacuum region was then extended beyond the attractive wall and the piston to ensure sufficient space between periodic images of the system along the z-direction. Periodic boundary conditions were applied in all three directions. The final dimensions of the simulation box were a = 6.4064 nm, b = 6.4064 nm, and c = 150 nm (Figure S18).

For studying the evaporation of water molecules from a BLVI, initially, a box with 42650 water molecules was equilibrated to a temperature of 25 °C (298 K) and pressure of 1 bar. The dimensions of this water box after equilibration were a = 6.4064 nm, b = 6.4064 nm, and c = 36 nm. The longest dimension of this water box was then extended by 10 nm on both sides of the water film and attractive walls were placed at the two ends of this box. A vacuum region was then extended beyond the attractive walls and the dimensions of the simulation box periodically repeated in three directions are a = 6.4064 nm, b = 6.4064 nm, and c = 500 nm (Figure S19).

All atoms of the FNPGs except the functional groups terminating the nanopores were fixed in their respective atomic positions throughout the simulation. All our simulations were carried out with the TIP4P-Ew (54) water model since it captures a broad range of properties of water, significant to our study (Note S17). SHAKE algorithm was used to fix the bond angle and bond lengths of the water molecules. All-atom optimized potentials for liquid simulation parameters were used for the FNPGs along with the computed charges. Nonbonded interactions were modeled by using dispersive forces.
and electrostatic forces. van der Waals interactions were modeled using Lennard–Jones potential with a cutoff of 1.2 nm. We use the Lennard-Jones interaction parameters developed by Werder et al. where the water–carbon interaction potential was parametrized to reproduce a water contact angle of 42°.86,87 Given the large variation in water contact angles reported for graphene,88 and the different parameters used in molecular dynamics simulations of water on graphene, we tested the influence of the Lennard-Jones interaction energy parameters (Note S18) on the evaporation flux. For the smallest OH terminated pores (d_H = 0.338 and 0.454 nm) where the interaction with carbon atoms is expected to be the greatest, we found that carbon–water interaction energies in the range of e = 0.392 to 0.65 kJ/mol, had a negligible effect on evaporation flux (Figure S41 and Table S23). Note that the highest interaction energy of 0.65 kJ/mol was used to include the effect of a single graphene sheet. Lorentz–Berthelot mixing rules were applied for the cross-interaction parameters for the Lennard–Jones potential between other unlike pairs. Particle–particle particle-mesh (PPPM) algorithm89 was used to compute the long-range electrostatic interactions with a cutoff of 1.0 nm for real space force calculations. Leap frog algorithm was employed to integrate the equations of motion with a time step of 1 fs. The temperature was maintained at 298 K (25 °C) using the Nose–Hoover thermostat with the time constant of 0.1 ps. First, the system was equilibrated for 10 ns, and then the production run was done for 500 ns. The trajectories of water molecules were stored at every 2 fs to analyze various structural and dynamical properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c07193.

Supplementary Notes, supplementary characterization images, other characterization data, schematic of the experimental setups, detailed simulation parameters and calculations (PDF)

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Author Contributions

W.L. and A.R. contributed equally to this work and share an equal lead authorship. W.L. performed experiments and data analysis. A.R. performed DFT and MD simulations along with the data analysis and result interpretation of these simulations. L.F.V. and M. D. performed the AC-HRTEM imaging. W.L., S.H., M.M. and K.H. performed XPS measurement. K.G.A. and K.V.A. supervised the studies. W.L., A.R., K.G.A. and K.V.A. wrote the paper with inputs from all authors.

Notes

The authors declare no competing financial interest.

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