***Supporting information for:***

**Light controls edge functional groups to**

**enhance membrane permeability**

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1. **Simulation model and method**



**FIG. S1 | Side (a) and top (b) views of the schematic representation of simulation systems, where confined water permeates through a graphene oxide (GO) membrane consisting of two stacked GO layers with an interlayer spacing of 0.78 nm. The blue, red, and white balls represent the carbon, oxygen, and hydrogen atoms on the membrane, respectively. The red and blue arrows indicate the electric and magnetic components of the EM stimulus, respectively.**

As shown in Fig. S1, the GO membrane model consists of two sheets of GO layers stacked in parallel, whose length, width, and interlayer spacing are 3.42, 5.11, and 0.78 nm, respectively. All atoms in the carboxyl were characterized by the Lennard-Jones parameters with a potential well depth (*ε*) and a van der Waals radius (*σ*) while the charges (*q*) are taking reference from amino acid ASPH.

**TAB. 1 | Potential well depth, van der Waals radius, and particle charge to parameterize the carboxyl on the GO membrane.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameters | C | O | O | H |
| *ε* (nm) | 0.375 | 0.296 | 0.3 | 0 |
| *σ* (kJ/mol) | 0.43932 | 0.878 | 0.711 | 0 |
| *q* (e) | 0.52 | -0.44 | -0.53 | 0.45 |

The membrane was centered in the simulation box with the initial side lengths of *L*X = 5.7 nm, *L*Y = 5.1 nm and *L*Z = 3.78 nm, indicating that water molecules can only permeate across the membrane in the *x*-direction. The box was filled with SPCE-modeled [1] flexible water molecules. Water molecules inside the GO membrane were denoted as confined water. Water molecules outside the membrane were denoted as bulk water.

All simulations were performed using the software GROMACS 5.1.4 [2]. The OPLS/AA force field was applied to treat the interaction between atoms, where the Lennard–Jones parameters between different atoms were calculated using the geometric average method. In the process of simulations, we firstly performed pre-simulations of each system lasting 100 ns with an isobaric-isothermal ensemble, which keeps the reasonable densities of bulk and confined waters. Next, we employed the configuration sampling to obtain the information of locations and momenta, and then switched to a canonical ensemble to explore the permeability of the membrane. The Nose-Hoover thermostat [3-4] was used to maintain the system temperature at a given number of 300K. Furthermore, to investigate the effect of hydrostatic pressure on the permeability of the membrane, we used the accelerate function of GROMACS to generate desired pressure difference () [5-6], which is related to the applied force () exerted on each water molecule based on the equation:

, (1)

where is the area of one side of the simulation box that is perpendicular to the water flow direction (the *x*-axis) and *n* refers to the total number of water molecules in the simulation box. The periodic boundary conditions were applied in all directions. Each simulation was performed 100 ns with a time step of 1 fs. The trajectory of all atoms was extracted for analyzing the permeation and spectrum with an interval time of 1 ps and 1fs, respectively.



**FIG. S2 | The temperature fluctuation of simulation systems under the 44.0 THz EM stimulus with different strengths *A*.**

In addition, a nose-hoover thermostat with a time constant for coupling of 0.2 ps was applied to take the excess injected energy away, maintaining the system temperature to fluctuate around the reference temperature. As shown in Fig. S2, we can see that the average system temperatures were maintained at 300 K regardless of the strength of the EM stimulus.

1. **The effect of 50 MPa pressure difference and 44.0 THz on the flow and flux of water.**



**FIG. S3 |** **The flow and flux of confined water in the presence of gradient field with 50 MPa pressure different and 44.0 THz EM stimuli.**

In experiment and industry application, the maximum osmotic pressure used for water purification is on the order of 10 MPa. In order to make the phenomenon more obvious, theoretical researchers usually prefer to employ a higher value of osmotic pressure for simulation. During the simulation, we applied an acceleration upon the water molecules to simulate the pressure and fixed the graphene. Therefore, the applied gradient field failed to buckle the bilayer structure. However, to prove the validity of our proposal under low osmotic pressure, we performed a series of simulations under *ΔP* = 50 MPa. As shown in Fig. S3, we can see that when the stimulus strength *A* increased, both the *F*flow and *F*flux were enhanced, while they are less than the value in the cases under *ΔP =* 500 MPa.

1. **Vibration spectra of different membrane models**



**FIG. S4 | The frequency of functional groups on different membrane model**s**.** **a)** The vibration frequency of hydroxyl groups on the membrane with characteristic peaks of 35.0 THz and 114.0 THz which deviates from those of bulk and confined water. **b)** The vibration frequency of epoxy on the membrane with characteristic peaks of 31.0 THz which deviates from those of bulk and confined water.

1. **The effect of 35.0 THz EM stimulus on the water flow and flux**



**FIG. S5 | The permeability of the GO membrane under 35.0 THz EM stimulus at different strengths *A*.** The phenomenon and mechanism of 35.0 THz EM stimuli to carboxyl are consistent with 44.0 THz EM stimuli.

1. **The estimation of injected power from light on water**



**Fig. S6 | The temperature change with respect to time under 44 THz EM stimulus at different strengths. When the strength of the stimulus is fixed, the temperature change is independent of the water box volume. a)** The results under the box size of 5×5×5 nm. **b)** The results under the box size of 8×8×8 nm.

To estimate the power of injected energy from the 44.0 THz EM stimuli to the unit volume of the system, we turned off the thermostat and tested different strengths of the EM stimuli. We can calculate the power by means of the formula

, (2)

where *m* is the mass of the water box, *c* denotes the specific heat capacity, ∆*T* is the change of the temperature, ∆*t* is the duration and *V* is the volume of the system. According to the change of system temperature with respect to the time (Fig. S6), we estimated the powers of 44.0 THz EM stimuli at the strength of 0.6 V/nm, 1.0 V/nm, and 1.5 V/nm are 0.06×10-9, 0.26×10-9, and 0.6×10-9 W/nm3, respectively.

1. **The effect of THz EM stimulus on the kinetic energy distribution**



**FIG. S7 | The comparison of the kinetic energy distribution of water molecules under normal condition and the case with 44.0 THz EM stimulus at the strength of 1.5 V/nm.**

In order to exclude the thermal effect-induced permeation enhancement, we should take the injected energy away in time using a thermostat. During the simulation, a nose-hoover thermostat with a time constant for coupling of 0.2 ps plays the role to maintain the system temperature stable. The smaller the time constant, the faster the injected energy is taken away. As discussed in Fig. S2, the average system temperature is maintained at 300 K, meaning that the permeation enhancement is not attributable to the temperature deviation-induced kinetic energy enhancement. Our further kinetic energy distribution analysis also shows that the distribution in the case under 44.0 THz EM stimulus at the strength of 1.5 V/nm is the same as the one in the case without stimulus (Fig. S7).

1. **The effect of modification rate on the water permeation**

In the process of modeling, the position of carboxyl groups was randomly functionalized on the edge of the membrane. We performed additional simulations to study the effect of edge functional group number on the permeation, where the groups were also randomly functionalized. The simulation results show that the permeability of the membrane decreases with the reduction of the number of functional groups (Fig. S8). Considering that the interaction between the THz EM stimulus and the groups can lower the energy barrier of the membrane, the reduction of group number decreases the proportion of the THz effect on the membrane function.

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**FIG. S8 | The relationship between the functional group modification rate and permeation. Herein, the modification rate is the ratio between the group number and the edge carbon atom number.**

1. **The THz EM stimulus effect on the water molecules’ distortion**

To show the water molecules’ distortion, we compared the probability distribution of intramolecular angle and bond length between the case under normal condition and the case under 44.0 THz EM stimulation at the strength of 1.5 V/nm. As shown in Fig. S9, we can see that the stimulation has a trivial effect on the structure of water molecule. This is because 44.0 THz is the resonance frequency of the C-O stretching of the carboxyl group rather than the vibration of a water molecule. As a result, EM stimulation with this frequency has limited effect on the dynamic property of water molecules.



**FIG. S9 | Distortion of water molecule under 44.0 THz EM stimulation at the strength *A* = 1.5 V/nm. a)** For the flexible water molecule model,the comparison of the probability distribution of intramolecular angle *α* between the caseunder normal condition and the case under 44.0 THz stimulation. **b)** The comparison of the probability distribution of hydrogen-oxygen bond length between the case under normal condition and the case under 44.0 THz stimulation.

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