

Supplementary Material for
Computational-simulation-driven discovery of novel zeolite-like
carbon materials as seawater desalination membranes

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S1. The Structure Concept of BEC-style ITQ-14 Zeolite

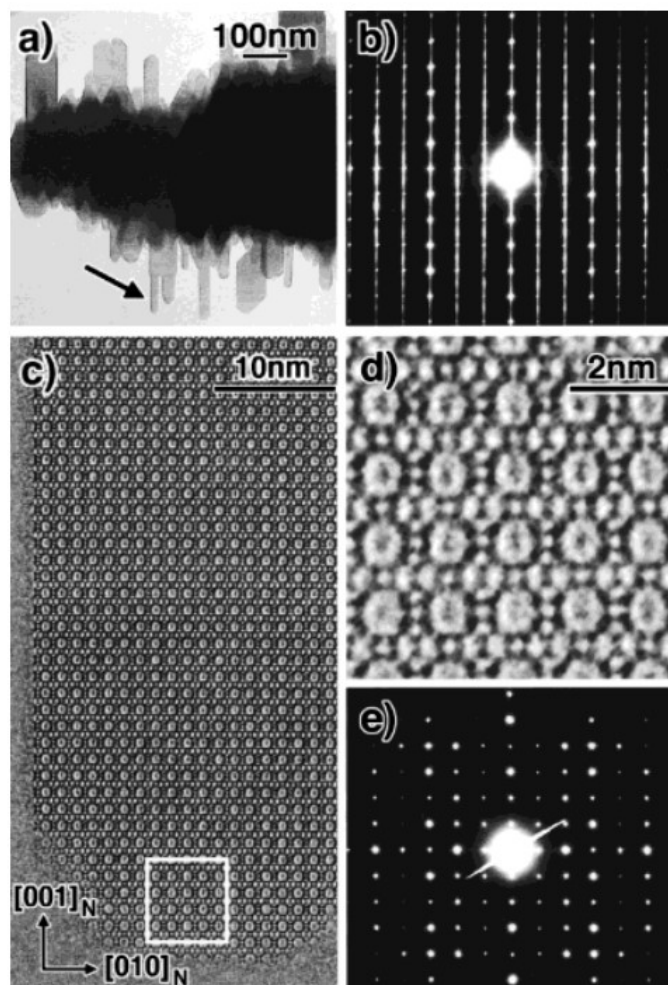


Fig. S1. (a) Low-magnification TEM image, (b) electron diffraction pattern (showing very strong diffuse line corresponding to the coexistence of polytypes A and B), (c) HREM image of the overgrown crystal along $[100]_N$, (d) an enlarged image of a part of (c), and (e) ED pattern of the overgrown crystal.

Pure silica ITQ-14 zeolite was prepared using tetramethylene bisquinuclidinium diquaternal cation (M_4BQ^{2+}). This organic cation was prepared at room temperature by reaction of 1,4- dibromobutane (4 mol, Aldrich) with quinuclidine (9 mol, Aldrich) using ethanol as a solvent. The mixture was stirred for 3 days before the solvent was evaporated under vacuum, and the resultant solid was washed with ethyl acetate and diethyl ether. The obtained dibromide dihydrated salt was then exchanged to the dihydroxide form by anion-exchange with Dowex-1 strongly alkaline resin (around 95% exchange).

For the zeolite synthesis tetraethyl orthosilicate (TEOS, Merck) was added to an aqueous solution of $M_4BQ(OH)_2$, and then the mixture was stirred at room temperature for an extended period of time to allow complete evaporation of the ethanol produced plus the water needed to reach the desired final composition. Then, the required amount of HF (aqueous solution recently titrated, typically 45-48 wt %) was added, and the mixture was homogenized by hand stirring. The mixture was poured into a Teflon-lined stainless steel autoclave and was then heated at 175 °C for 12 days while being tumbled (60 rpm). The gel composition was $SiO_2:0.25 M_nBQ(OH)_2:0.50 HF:7.5 H_2O$.

After cooling the autoclaves, the contents were filtered, and the recovered solid was washed with water and dried. According to chemical analysis, the material contains 3.5 F⁻ per 64 SiO₂. Recently, the existence of D4R in pure ITQ-14 was claimed from the chemical shifts in F MAS NMR of -39.3 ppm which were assigned to F located in D4R.

Reference

Liu Z, Ohsuna T, Terasaki O, et al. The first zeolite with three-dimensional intersecting straight-channel system of 12-membered rings[J]. Journal of the American Chemical Society, 2001, 123(22): 5370-5371.

S2. Structural Screening

S2.1 Data preparation

All structural data of the 2D zeolite-like carbon materials were obtained by applying the CALYPSO structure prediction method developed by Ma's group, which is grounded on the ML particle swarm optimization algorithm to explore and predict functional materials on demand. In the structural prediction, the number for the C atom in one formula unit was 12, and the maximum number of formula units per cell was 2. Also, the primary estimated volume per formula unit was 20 \AA^3 and the prediction generation was 50. In addition, the population size of the predicted structures was 40 in every generation, and the proportion of randomly generated structures in each generation was 40%. It should be noted that our CALYPSO crystal structure prediction method was interfaced with the Vienna ab initio simulation package (VASP), and each generated structure was optimized thrice to ensure accurate calculation.

S2.2. Machine learning models

Enriching the π -bonds and building multiple carbon ring structures rationally should be an active solution to regulate the mechanical properties and electronic structure. All data of the original dataset were split into 70% training and 30% test sets. The training set was used to optimize and train the model through cross-validation, while the test set was employed to evaluate the accuracy of the trained model. We trained each ML model utilizing a 5-fold cross-validated grid search to optimize the hyperparameters, i.e., dividing the data into five random groups and

training the model with four of the five subsets, then evaluating the remaining subsets. The process was repeated for each of the five divisions as the test set, after which the predictive ability of the model was evaluated as the average performance of the model over all replications. This is done so that each segmented dataset is treated as a test set for the iteration. Neural networks (NN) have been extensively applied for predicting material properties and accelerating simulation to assist material characterization due to their advantages of self-learning, associative storage, and the ability to find optimization solutions at high speed. Numerical features such as energy density, adsorption energy, and mechanical properties were renormalized and served as the input feature vectors for the NN model. The correlation between the energy density and the pore size features of 2D membranes was first established using the NN model, which consists of an input layer, an output layer, and two totally connected hidden layers, and the size of the hidden layers was determined by applying the grid search method. Among them, the input characteristics of the NN input layer are $E \leq -8.5$ eV/atom. In addition, we have selected the layer magnitude parameter set to 100 for the hidden layers. The mean squared errors and the rectified linear unit were adopted as the lost function and activation function, respectively. The root mean absolute error (MAE) of the test set measured on the model was 0.25%, and the coefficient of determination (R^2) value was 0.96. Based on the similar operation described above, the adsorption energy and mechanical properties of the suitable pore size were further screened (the input characteristics of the NN input layer were $U < -0.5$ eV and $C(\theta) > 32$ GPa and $v(\theta) > 0.25$, respectively).

S2.3 Structural screening

Some crucial eigenvectors are considered during training: (i) The total energy released by forming the structure is applied as a physical parameter to determine the structural stability. The criterion for obtaining a stable structure is defined as the total energy $E \leq -8.5$ eV/atom after referring to the stability of numerous graphene-based materials; (ii) The pore size is an essential indicator for desalination properties. According to previous studies, a pore size of 0.45–0.55 nm can display excellent desalination efficiency, and the corresponding carbon rings in the carbon density model should contain 10–12 carbon atoms; (iii) To ensure the strength and integrity of the structure during desalination, the Young's modulus C and Poisson's ratio ν act as descriptors of the mechanical properties, and the screening terms are set to $C(\theta) > 32$ GPa and $\nu(\theta) > 0.25$; (iv) The best-fitting algorithm for the training set is employed to predict the adsorption energy of a Na^+ at a hollow site. For stable adsorption, the screening judgment of $U < -0.5$ eV is performed empirically; (v) Finally, we have to evaluate the preparation possibilities of the structures. The determination criteria for the structural screening are shown in Fig. S2.

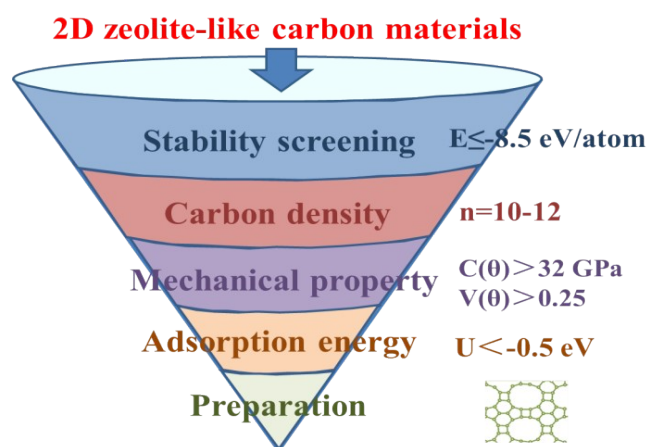


Fig. S2. Determination criteria for structural screening.

Specifically, the stability screening data are plotted in Fig. S3. The magenta line indicates $E = -8.5$ eV/atom, whereas the blue and red dots represent the structure subsets that do not fulfill and satisfy the screening criteria in the unit cell, respectively. We treated 292 2D carbon nanomaterials and obtained 52 target spots ($E \leq -8.5$ eV/atom) according to the stability criteria, which can be assumed as stable unit cells to be further investigated.

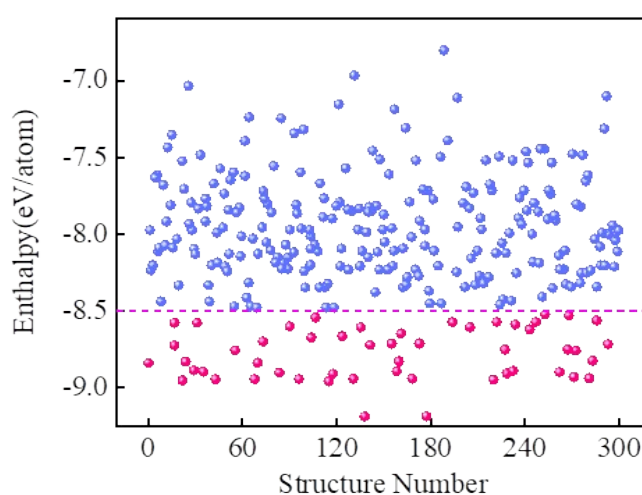


Fig. S3. Stability screening of machine learning.

Fig. S4 illustrates the correspondence between carbon density and total energy of feasible stable structures. They are based on the constructed carbon density model used to further search for the structures that match the screening eligibility. The structures of the largest pores, containing 7–9, 10–12, and 14–18 carbon atoms in the unit cell, are represented with yellow, red, and blue dots, respectively. The energy values corresponding to the pore structures constructed with different amounts of carbon atoms are further summarized in the embedded diagram. We searched for some stable structures incorporating 10- to 12-membered carbon rings, where the 10-membered carbon ring structures have energies in the range of -8.372 to -8.830

eV/atom. Similarly, the 12-membered carbon ring structures have energy values between -8.501 and -8.600 eV/atom.

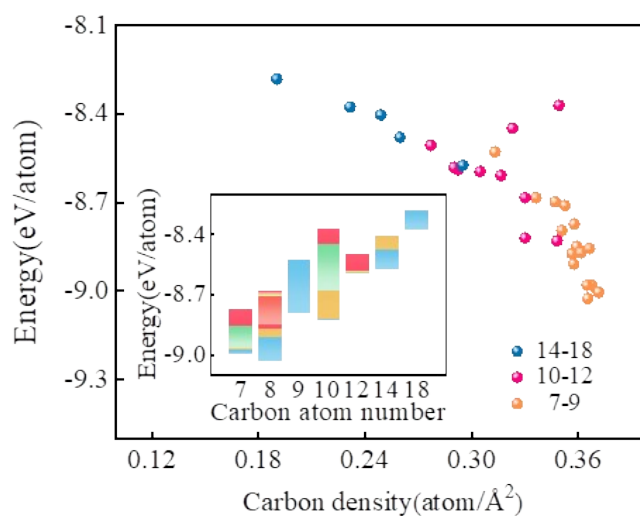


Fig. S4. Correspondence between carbon density and total energy.

These structures have been further screened for mechanical properties and adsorption energy. Finally, based on the results of the screening, a main target was chosen for subsequent simulation validation in this paper to explore the universal characteristics of desalination membrane structures. Therefore, ML provides a possible solution for developing 2D carbon membranes for seawater desalination.

S3. The Calculations Details of Classical Molecular Dynamics

S.3.1 Establishment of seawater desalination system model

All the molecular dynamics simulations were carried out using the LAMMPS package. The SPE/C water model was adopted for the explicit solvent. The long-range electrostatic interactions were treated by the Particle Mesh Ewald method, and a typical distance cutoff of 12 Å was used for the van der Waals interactions. The non-bonded interaction pair list was updated every 10 fs. In order to place strain on the Zeo-C filter, the cross section along the x-y plane in the simulation box was fixed at a certain value. Canonical sampling was performed through the velocity rescaling method at constant temperature of 1000 K. An integration time step of 1 fs was used for all simulations. The simulation box contains 5150 water molecules, 93 Na⁺, 93 Cl⁻, a Zeo-C filter, and an ideal single graphene sheets used as a piston. The system was firstly equilibrated with z-direction pressure coupling at 1atm for 10 ns, followed by 30 ns productive simulations under a given constant piston pressure in the otherwise NVT ensemble.

S.3.2 Script of the movement of ions in the electric field

```
#!/perl

use strict;

use Getopt::Long;

use MaterialsScript qw(:all);

my $doc = $Documents{"packmol- Zeo-C.xsd"};

Modules->Forcite->ChangeSettings([
```

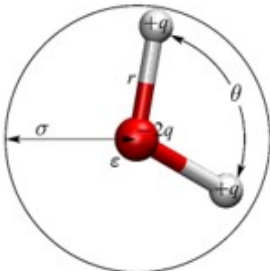
```
ElectricFieldStrength => 1,  
  
ElectricFieldX => 0,  
  
ElectricFieldY => 0,  
  
ElectricFieldZ => 1,  
  
CounterElectricField =>"No"]);  
  
my $results = Modules->Forcite->Dynamics->Run($doc, Settings(  
  
    Quality => 'Medium',  
  
    CurrentForcefield => 'Universal',  
  
    ChargeAssignment => 'Use current',  
  
    Ensemble3D => 'NVT',  
  
    TrajectoryFrequency => 100,  
  
    AssignFixedBonds => 'No'));  
  
my $outTrajectory = $results->Trajectory;  
  
my $results = Modules->Forcite->Dynamics->Run($doc, Settings(  
  
    ChargeAssignment => 'Use current',  
  
    Ensemble0D => 'NVT',  
  
    Ensemble3D => 'NVT',  
  
    Temperature => 300,  
  
    NumberOfSteps => 8000,  
  
    TrajectoryFrequency => 8000));  
  
my $outTrajectory = $results->Trajectory;
```

S3.3 SPC/E all-atomic water model and force field parameter setting

(1) LJ potential calculation formula :

$$U = \sum_i \sum_{j>i} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_i \sum_{j>i} k \frac{q_i q_j}{\dot{r}_{ij}}$$

Table S1. Parameters of SPC/E model for water molecules

Parameters	Values	SPC/E water molecule model
ϵ (kcal/mol)	0.1553	
σ (Å)	3.166	
R(Å)	1	
θ (°)	109.47	
q(q)	(±)0.4238	

(2) LJ potential parameters

The parameters are summarized in Table S2.

Table S2. LJ and charge parameters employed in this work

Element	C_{piston}	$C_{\text{Zeo-C}}$	H_w	O_w	Cl^-	Na^+
ϵ (kcal/mol)	0.1050	0.1050	0.0	0.1553	0.0128	0.3526
σ (Å)	3.8510	3.8510	0.0	3.1656	2.1600	4.8305
q(e)	0.0	0.0	0.4238	-0.8476	-1.00	1.00

(3) Core code :

Mass :

Ow 15.9994

Hw 1.008

Charge :

Ow -0.8476
Hw 0.4238
pair_style lj/cut/coul/long 9.0
pair_coeff 1 1 0.1553 3.166 # 1=Ow, 2=Hw
pair_coeff 1 2 0 0
pair_coeff 2 2 0 0
bond_style harmonic
bond_coeff 1 0.0 1.0 # 1=Ow-Hw
angle_style harmonic
angle_coeff 1 0.0 109.47 # 1=Hw-Ow-Hw
kspace_style pppm 1.0e-4
fix 1 watergroup shake 0.0001 20 0 b 1 a 1

S4. The Self-cleaning Property of Zeo-C

S.4.1 The calculations details of the self-cleaning property

Simulation were carried out by Forcite module of commercially available software Materials Studio (Accelrys Software Inc.). Forcite do not support such kind of calculation (Applying an electric field in modelled structures) but it has embedded PERL interpreter. Thus, the procedure of simulation combined with the electric field was carried out by PERL script language. In order to describe interatomic bonds and non-bonding potential energy, the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomic Simulation Studies) force field was used for simulations. Next, the structures were equilibrated by thermostat at desired temperature (300 K) during 100 fs. Such time is required to achieve uniform temperature distribution for the model, time step of simulation was set at 1 fs. The NVT ensemble was used at the next step. From this moment to the end of simulation (till 10 ps) at every time step (1 fs) and the constant value (1 V/Å), electric field strength was added along the electric field direction vector Z component.

S5. The POSCAR file of Zeo-C

Zeo-C

1.0

7.2100000381	0.0000000000	0.0000000000
0.0000000000	6.0199999809	0.0000000000
0.0000000000	0.0000000000	15.0000000000

C

14

Direct

0.101630002	0.877770007	0.500000000
0.898370028	0.122229993	0.500000000
0.898370028	0.877770007	0.500000000
0.101630002	0.122229993	0.500000000
0.287160009	0.194930002	0.500000000
0.712839961	0.805069983	0.500000000
0.712839961	0.194930002	0.500000000
0.287160009	0.805069983	0.500000000
0.398930013	0.379709989	0.500000000
0.601069987	0.620290041	0.500000000
0.601069987	0.379709989	0.500000000
0.398930013	0.620290041	0.500000000
0.403290004	0.000000000	0.500000000
0.596709967	0.000000000	0.500000000

S6. The Applied Pressures of Other 2D Materials

The pressure values required to achieve 100% salt rejection for other 2D materials have been identified from the extensive literature and are listed in the table below.

Table S1. The pressure values required to achieve 100% salt rejection for other materials

References	Materials	Pressure (MPa)
[1]	Nanoporous graphene	125
[2]	Graphene kirigami	100
[3]	Carbon nanocones (CNCs)	100
[4]	Single-layer Metal–Organic Framework Membranes	100
[5]	Nanoporous graphitic carbon nitride membranes	60
[6]	Nanoporous Boron Nitride Nanosheet Membranes	50
[7]	layer-stacked black phosphorus carbide (α -PC) membrane	40
[8]	Zeo-C membranes	70

[1] Nano letters, 2012, 12(7): 3602-3608.

[2] Carbon, 2022, 195: 183-190.

[3] Carbon, 2018, 129: 374-379.

[4] Nano Letters, 2019, 19(12): 8638-8643.

[5] Journal of Membrane Science, 2021, 620: 118869.

[6] The Journal of Physical Chemistry C, 2017, 121(40): 22105-22113.

[7] Desalination, 2022, 522: 115422.

[8] This work.

Dynamic simulation of seawater desalination

See Appendix 1.

Dynamic simulation of self-cleaning property

See Appendix 2.