Appendix A: Supplementary material

Graphene stimulating nucleation-and-growth rate of NaCl crystals via membrane crystallization

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S.1 Calculation of thermodynamics forces

The Lifshitz-van der Waals γ^{LW} (mJm⁻²), polar γ^{AB} (mJm⁻²), acid (electron acceptor) γ^{+} (mJm⁻²), base (electron donor) γ^{-} (mJm⁻²) components of the surface free energy γ_s (mJm⁻²) were calculated from averaged values of the contact angles estimated for three different liquid probes (Water, Glycerol and Diiodomethane) according to Good, van Oss and Chaudhury approach [1-2] :

$$\gamma_s^{LW} = \frac{\gamma_l^{LW} \cdot (1 + \cos\theta)^2}{4}$$
eq.1

$$\gamma_l \cdot (1 + \cos\theta) = 2 \cdot \left(\sqrt{\gamma_s^{LW} \cdot \gamma_l^{LW}} + \sqrt{\gamma_s^+ \cdot \gamma_l^-} + \sqrt{\gamma_s^- \cdot \gamma_l^+} \right)$$
eq.2

$$\gamma_s^{AB} = 2 \cdot \sqrt{\gamma_s^+ \gamma_s^+}$$
 eq.3

and the free energy of interfacial interaction W_{iwi} (mJm⁻²) and the work of interfacial attraction W_{iwi} (mJm⁻²) were calculated according to these relations:

$$W_{iw} = 2\left(\sqrt{\gamma_i^{LW}\gamma_w^{LW}} + \sqrt{\gamma_i^+\gamma_w^-} + \sqrt{\gamma_i^-\gamma_w^+}\right)$$
eq.4

$$W_{iwi} = 2\left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 + 4\left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_w^+ \gamma_w^-} - \sqrt{\gamma_i^+ \gamma_w^-} - \sqrt{\gamma_i^- \gamma_w^+}\right)$$
eq.5

where i is the membrane surface, w the liquid water.

S.2 Build up of simulated systems

The Material Studio package (version 7.0) of Accelrys [3] and the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field [4] were used for the simulations of the pristine PVDF and for PVDF/G composite membrane models. The PVDF template chain for the initial packing with the Amorphous Cell module consisted of 100 monomers (602 atoms) and every packing model contained 13 polymer chains. Thus, a total of 7826 atoms were grown in a 2D model under periodic boundary conditions for the pristine PVDF. For PVDF/GP systems, each graphene platelet contained 162 atoms with a dimension of (1.5x2.55) nm². Three and six graphene sheets were used in PVDF/GP5 and PVDF/GP10, respectively.

Temperature was set at 298 K. A final density of 1.7 ± 0.015 g/cm³ for pristine PVDF was obtained and agrees with the value of 1.68 g/cm³ of the PVDF polymer experimentally used (SOLEF 60/20; Solvay Specialty polymers, IT) and as in reference [5]. The values of 1.77 ± 0.0106 g/cm³ for PVDF-G 5 wt % and of 1.78 ± 0.084 g/cm³ for PVDF-G 10 wt %, were obtained, respectively.

More details on the method for packing and equilibration can be found in Tocci et al. [6].

All MD simulations, both considering only the bulk solution and with the polymeric membrane models, were then performed using the GROMACS software package, version 5.1.4 [6-10]



Figure S1 Final box for PVDF/GP membranes extended with Gromacs software.

The force field parameters of the PVDF polymer developed by Byutner and Smith [6] were used in this study and are listed in Table S1.

Bonds				b_{ij}		$k^{\scriptscriptstyle b}_{ij}$	
				(nm)	(kJ/i	mol nm²)	
CH–H			0.1085		274135.68		
CF–F			0	0.1357		417814.24	
CF–CH			0.1534		258487.52		
Angles			$oldsymbol{ heta}_{ijk}^{0}$			$k^{ heta}_{_{ijk}}$	
			(deg)		(kJ/mol rad ²)		
F-CF-F			1	105.27		1004.1600	
F–CF–CH			107.74		75	753.1200	
CH–CF–CH			1	118.24		671.9504	
H–CH–H			1	109.27		322.1680	
H–CH–CF			1	108.45		358.9872	
CF–CH–CF		118.24		671.9504			
Torsions	$k_{\phi}(1)$	$k_{\phi}(2)$	$k_{\phi}(3)$	$k_{\phi}(4)$	$k_{\phi}(5)$	$k_{\phi}(6)$	
(kJ/mol)							
CF-CH-CF-CH	1.65268	3.01248	-1.58992	-0.85772	1.77820	-0.10460	
F-CF-CH-CF	1.48532	1.44348	-1.58992	0.58576	0.60668	-0.10460	

Table S1. Force field parameters for polyvinylidene fluoride (PVDF) [11,12]

The size of the PVDF and PVDF/GP5-G10 models were of (5.63x5.63x11.38) nm³ for pristine PVDF; of (5.55x5.55x10.90) nm³ for PVDF-G5 and (5.71x5.71x10.91) nm³ for PVDF-G10. The simulation boxes were filled with 7637, 6989 and 7194 SPC/E water molecules, respectively [10]. Slightly supersaturated conditions were considered with a concentration of solutions of about 6 M with almost 759 - 800 pairs of Na⁺ and Cl⁻ ions chosen in order to simulate the condition near a membrane surface during crystallization experiments. The ion parameters with the OPLS force field [13] were used. All pair interactions consisted of Lennard-Jones (LI) and Columbic terms, and the Lorentz–Berthelot combining rules [14] were chosen to generate LI parameters between different types of atoms. Other LI parameters utilized in this study are shown in Table S3. The total energy of the materials is [6-8]

$$V = \sum_{i,j} \frac{1}{2} k_{ij}^{b} \left(r_{ij} - b_{ij} \right)^{2} + \sum_{i,j,k,l} \frac{1}{2} k_{ijk}^{\theta} \left(\theta_{ijk} - \theta_{ijk}^{0} \right)^{2} + \sum_{i,j,k,l} \sum_{n} \frac{1}{2} k_{ijkl}^{\phi} \left(n \right) \left(1 + \cos \left(n \phi_{ijkl} - \phi_{s} \right) \right)$$

$$+ \sum_{i>j} 4 \varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \sum_{i>j} \frac{1}{4 \pi \varepsilon_{0}} \left(\frac{q_{i}q_{j}}{\varepsilon_{r} r_{ij}} \right)$$
eq.6

where r_{ij} , θ_{ijk} , and ϕ_{ijkl} are the distance, angle, and torsional angle between the bonded atoms i and j, i, j and k, i, j, k, and l, respectively. ϕ_s is 1800. ε_{ij} and σ_{ij} are the well depth and size of Lennard-Jones. ε_0 is the permittivity of vacuum, and ε_r is the relative dielectric constant, and in this case, it is 1. q_i and q_j are the respective charges of atoms i and j. Other LJ parameters utilized in this study are shown Table 3. Periodic boundary conditions were applied. Long-range Columbic interactions were calculated using the particle-mesh Ewald (PME) summation method [15]. The cutoff radius for LJ interactions and for short-range Columbic interactions was set to 1 nm. The simulations were conducted in the isothermal–isobaric ensemble (NPT) at 300 K and 1 atm using the velocity rescaling thermostat ($\tau t = 0.1$ ps) for temperature coupling and the Berendsen barostat [16] with the compressibility of 4.5 × 105 bar⁻¹ ($\tau p = 1$ ps) for pressure coupling. The initial configuration for the models were obtained by minimizing the total energy in the box, then equilibrated via isothermal ensemble (NVT) followed by NPT for each 2000 ps with a time step of 0.2 fs. Finally, the systems were carried out with a production run of 200 ns. All trajectories were visualized using Visual Molecular Dynamics, version 1.9.3 [17].

Table S2. Nonbonded force field parameters and charges of the Lennard-Jones potential for water, ion, and PVDF^a.

Atom	σ	3	Charge
Туре	(Å)	(kJ/mol)	(e)
Ow	3.166	0.6501	-0.847600
Hw	0.0	0.0	+0.423800
Na ⁺	3.330	0.0116	+1
Cl-	4.417	0.4928	-1
C _{PVDF, H}	3.500	0.2763	-0.650250
C _{PVDF, F}	3.500	0.2763	+0.765000
	2.500	0.1256	+0.225875
F _{PVDF}	2.983	0.2512	-0.283250

^a The O_w and H_w parameters are for water and from[10], and the Na⁺ and Cl⁻ parameters are from [18] and [19], respectively. The parameters of C_{PVDF, H}, C_{PVDF, F}, H_{PVDF}, and F_{PVDF} are for PVDF and from [20]

Table S3. Theoretical parameters of membrane systems produced.								
System	V box	NaCl H ₂ O		NaCl initial				
		molecules	molecules	concentration				
	(nm³)	(nº)	(n ⁰)	(mol/L)				
PVDF	360.71	818	7637	6.020				
PVDF/GP5	335.74	750	6989	6.012				
PVDF/GP10	355.71	772	7194	6.004				

S.2 1.4 Analysis of simulated systems

The radial distribution function, g(r), related to specific interactions between the O of water molecules and the PVDF (red line in Figure 4b) and graphene (black line in Figure 4b), were calculated along with 200 ns of simulation time. The curve of g(r) indicates the local probability density of finding type B atoms at a distance r from type A atoms, averaged over the equilibrium density, and is defined by the equation [15]:

$$g(r) = \frac{n_B / 4\pi r^2 dr}{N_B / V}$$
eq. 7

where N_B is the total number of type B atoms, V is the total volume, n_B is the number of type B atoms lying at a distance r from atom A, considering a shell of thickness dr.

S.3 The Enthalpy of crystallization

The enthalpy of crystallization of NaCl is of 1.5 kJ per mole [21], it is an exothermic process with a very low rise in temperature of the system.

We have used a general procedure for crystallizing NaCl approaching a membrane [22]; however, the force field used, OPLS can give only qualitative explanations because it not been parameterized for distinguishing the energy of the crystallization process. Through the NPT simulations the temperature is kept constant together with the particle number and the pressure, but then the total energy of the system is no longer conserved. Consequently, the heat of crystallization affects the total energy of the system in such a way that kinetic energy stays constant, due to the constant temperature and the potential energy is decreased. Plotting the total energy along the simulation. There is not a sharp decline as nucleation starts, like it happens for KCl [23]. However, the descendent trend indicate that the simulation reached the equilibrium state and crystal nuclei are no more increased in size by addition of further ions. More detail on theoretical work can be found in [24].



S.4 Membrane Crystallization set up

Thermally-driven MCr experiments were executed accordingly with the Direct Contact (DC) configuration using 5.3 M NaCl solutions as a feed (Figure S2). All experiments were carried out at T_{feed} =36.5±0.5°C, Re_{feed} =9,253E+06 and $Re_{permeate}$ =3.368E+06.

Retentate and distillate streams were converged, in a counter-current way, via Peristaltic pumps (COLE PARMER - MASTERFLEX L/S) toward the membrane module containing the membrane,

where the liquid water was evaporated. The membrane module allocates 11.35 cm² of the tailored flat sheet membranes. Moreover, the fluid channel cross-area was equal to 0.24 cm², for a mean velocity equal to 0.17 and 0.07 m/s on feed and permeate side, respectively. The trans-membrane fluxes were estimated by evaluating the weight variations in the distillate tanks with a balance (Gibertini – EU-C LCD). Related values were estimated considering the effective free area and thickness of each membrane. Refrigerated bath (NESLAB RTE 17) and heater (FALC – SB15) provided the achievement and maintenance of the desired temperatures, both at retentate and permeate side. The salt conducibility of the feed and permeate streams were measured by using a conductive meter (HI 2300 bench meter-Hanna Instruments).

During the experiment, feed samples were extracted from the crystallization tank. Inlet and outlet of retentate solution from the crystallization tank were set in such a way to avoid dead zones and to guarantee the homogeneity of crystallization solution.

The produced sodium chloride crystals produced were observed by using an optic microscope (NIIKON, ECLIPSE LV100ND) and pictures recorded with a digital video-camera module DS-Fi2 equipped with optical head (10/100X).



Figure S2. Schematic representation of a membrane distillation/membrane crystallizer plant

S.5 Membrane crystallization equations

In MCr, the membrane provides an excellent support for heterogeneous nucleation. Morphological characteristics of the membrane stimulate the nucleation, when supersaturation is reached. This condition occurs more quickly as higher rate of water evaporation and diffusion takes place through the membrane. An indicator of the capacity of the membrane to transfer water vapour and, therefore, to concentrate the saline solution is the molecular trans-membrane flux (J), which is related to intrinsic morphological characteristics of the membrane and process parameters by the following equation:

$$J = \frac{\varepsilon PD_{ij}}{\tau \delta RT} ln \left(\frac{p^2 \frac{2r}{3} \left(\frac{8RT}{\pi M_i}\right)^{1/2}}{p^2 + PD_{ij}} \right) \left(\frac{p^2 \frac{2r}{3} \left(\frac{8RT}{\pi M_i}\right)^{1/2}}{p^2 + PD_{ij}} + PD_{ij} \right) \right)$$

eq.8

Where ε is the membrane porosity, P the total pressure, D_{ij} the diffusivity, τ the membrane tortuosity, δ the membrane thickness, R the ideal gas constant, T the temperature, r the pore size, M_i the molecular weight, p_a^1 and p_a^2 the partial pressure of air at feed and membrane surface, respectively.

It is evident that the membrane structural properties and operative conditions - i.e. temperature, concentration, flowrate - affect membrane crystallization performance in terms of solvent evaporation and diffusion rate and, consequently, in terms of crystals nucleation and growth.

It is also useful to say that a crystallizing solution is formed by a certain number of solute molecules, which move among the molecules of solvent and collide with each other, so that a number of them converge forming clusters. The critical size n^* , which an assembly of molecules must have in order to be stabilized by further growth, depends on the supersaturation, as hereafter reported:

$$n^{*} = \frac{32\pi v_{0} \gamma^{3}}{3(k_{B}T)^{2} ln^{3}S}$$
eq.9

where v_0 is the molecular volume, γ is the interfacial energy, k_B is Boltzmann's constant, S is the supersaturation.

Crystals nucleation and growth can be estimated according to the Randolph-Larson generalpopulation balance, which is valid for a steady-state crystallizer receiving solids-free feed and containing a well-mixed suspension of crystals experiencing negligible breakage (as in the case of MCr). In this context, a material-balance statement degenerates to a particle balance (the Randolph-Larson general-population balance); in turn, it simplifies to:

$$\frac{dn}{dL} + \frac{n}{Gt} = 0$$

Integrated between the limits n⁰, the population density of nuclei (for which L is assumed to be zero), and n, that of any chosen crystal size L, eq. 10 becomes:

$$\int_{n^0}^{n} \frac{dn}{n} = -\int_{0}^{L} \frac{dL}{Gt}$$
eq.11

$$\ln n = \frac{-L}{Gt} + \ln n^0$$
eq.12

where n is the crystal population density, L is crystal size, G is growth rate, t is retention time. A plot of ln n versus L is a straight line whose intercept is ln n⁰ and whose slope is -1/Gt. Thus, from a given product sample of known slurry density and retention time it is possible to obtain the nucleation rate and growth rate for the conditions tested when the sample satisfies the assumptions of the derivation and yields a straight line [25-26].

The evolution of particle size distribution as function of time allows evaluating the coefficient of nucleation (B₀) according to the equation describing the nucleation rate:

The coefficient of variation (CV) is estimated from:

$$CV = \frac{F_{80\%} - F_{20\%}}{2 \cdot F_{50\%}} \cdot 100$$
 eq.14

Where F is the cumulative percent function given by the crystal length at the indicated percentage. The variation coefficient (CV) is defined as the ratio of standard deviation to mean value and it is an industrially relevant parameter since it measures the scatter of crystal product size around its mean. Precisely, a low CV means a narrow crystal size distribution (CSD) curve.

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