Supporting Information for

Self-ordering of nontrivial topological polarization structures in nanoporous ferroelectrics

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I. Supplementary figures

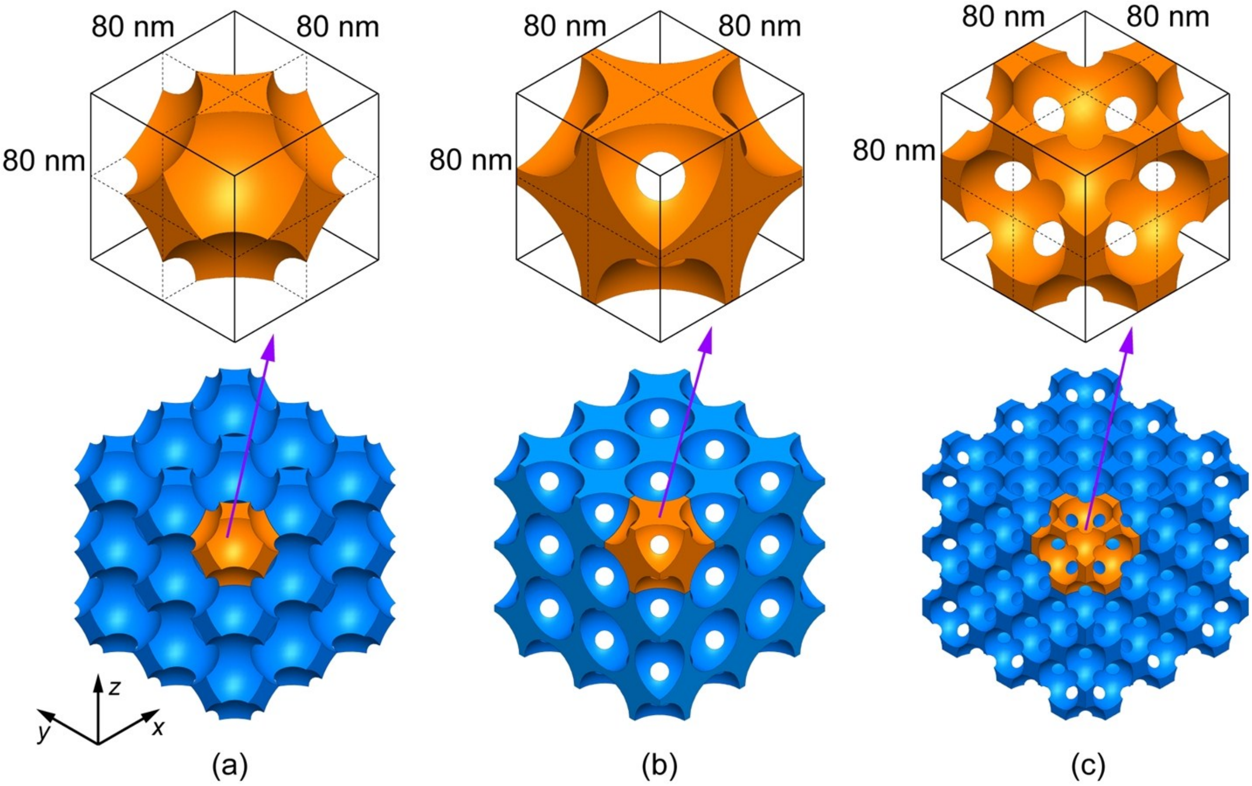

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Figure S1. Structures of open porous ferroelectrics and their building blocks appeared in pseudo-cubic: (a) simple cubic (SC), (b) body-centered cubic (BCC), and (c) face-centered cubic (FCC) arrangements of spherical pores. The periodic boundary conditions are applied to the x, y, and z directions. The periodicity of the pseudo-cubic structure is taken to be 80 nm in the x, y, and z directions.

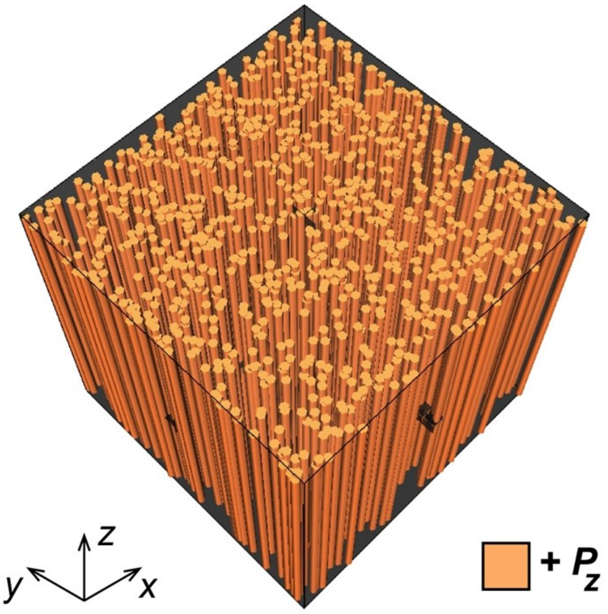


Figure S2. Rectilinear domain structure in ideal infinite dense ferroelectric material.

II. Phase field model

The spontaneous polarization configurations of ferroelectric nanoporous structures are investigated by using phase-field modelling based on the Ginzburg-Landau theory. In the phase-field model of ferroelectric materials, polarization vector, $\boldsymbol{P} = (P_x, P_y, P_z)$, is taken as the order parameter to describe free energies of the ferroelectric system. The total free energy of the ferroelectric system, F, can be described by [1]

$$F = \int_V f dV = \int_V \left(f_{Landau} + f_{Elastic} + f_{Coupling} + f_{Gradient} + f_{Electric} \right) dV \tag{S1}$$

where f_{Landau}, $f_{Elastic}$, $f_{Coupling}$, $f_{Gradient}$, and $f_{Electric}$ denote the Landau energy density, the elastic energy density, the coupling energy density, the gradient energy density, and the electrostatic energy density, respectively. V is the entire volume of the ferroelectric system.

The Landau energy density is expressed by a six-order polynomial of the spontaneous polarization as [2]

$$\begin{aligned} f_{Landau} &= \alpha_1 \left(P_x^2 + P_y^2 + P_z^2 \right) + \alpha_{11} \left(P_x^4 + P_y^4 + P_z^4 \right) \\ &+ \alpha_{12} \left(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2 \right) + \alpha_{111} \left(P_x^6 + P_y^6 + P_z^6 \right) \\ &+ \alpha_{112} \left[P_x^4 \left(P_y^2 + P_z^2 \right) + P_y^4 \left(P_x^2 + P_z^2 \right) + P_z^4 \left(P_x^2 + P_y^2 \right) \right] \\ &+ \alpha_{123} P_x^2 P_y^2 P_z^2 \end{aligned} \tag{S2}$$

where $\alpha_1 = (T - T_0) / 2\kappa_0 C_0$ is the dielectric stiffness, α_{11}, α_{12}, α_{111}, α_{112}, and α_{123} are higher order-stiffness coefficients, T and T_0 denote the temperature and the Curie-Weiss temperature, respectively, C_0 denotes the Curie constant, and κ_0 denotes the dielectric constant of vacuum. In general, the pure strain energy density is $f_{Elastic} = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$, where c_{ijkl} is the elastic stiffness tensor. The summation convention for the repeated indices is employed, and the Latin letters *i*, *j*, *k*, *l* take *1*, *2*, *3*. In addition, the notations of strain with indices 1, 2, and 3 are equivalent to that with indices *x*, *y*, and *z*, respectively. For a cubic material with its three independent elastic constants C_{11}, C_{12} and C_{44} in the Voigt's notation, the pure elastic energy can thus be rewritten as [3-6]:

$$f_{Elastic} = \frac{1}{2} c_{11} \left(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2 \right) + c_{12} \left(\varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{zz} \varepsilon_{xx} \right) + 2 c_{44} \left(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2 \right) \tag{S3}$$

where c_{11}, c_{12}, and c_{44} are the elastic constants. The coupling energy density is given by

$$\begin{aligned} f_{Coupling} &= -q_{11} \left(\varepsilon_{xx} P_x^2 + \varepsilon_{yy} P_y^2 + \varepsilon_{zz} P_z^2 \right) - 2 q_{12} \left[\varepsilon_{xx} \left(P_y^2 + P_z^2 \right) + \varepsilon_{yy} \left(P_x^2 + P_z^2 \right) + \varepsilon_{zz} \left(P_x^2 + P_y^2 \right) \right] \\ &- 2 q_{44} \left(\varepsilon_{xy} P_x P_y + \varepsilon_{xz} P_x P_z + \varepsilon_{yz} P_y P_z \right) \end{aligned} \tag{S4}$$

where q_{11}, q_{12}, and q_{44} are electrostrictive coefficients. The gradient energy density is given by

$$
\begin{aligned}
f_{Gradient} &= \frac{1}{2}G_{11}\left(P_{x,x}^2 + P_{y,y}^2 + P_{z,z}^2\right) + G_{12}\left(P_{x,x}P_{y,y} + P_{y,y}P_{z,z} + P_{z,z}P_{x,x}\right) \\
&+ \frac{1}{2}G_{44}\left[\left(P_{x,y} + P_{y,x}\right)^2 + \left(P_{y,z} + P_{z,y}\right)^2 + \left(P_{x,z} + P_{z,x}\right)^2\right] \\
&+ \frac{1}{2}G'_{44}\left[\left(P_{x,y} - P_{y,x}\right)^2 + \left(P_{y,z} - P_{z,y}\right)^2 + \left(P_{z,x} - P_{x,z}\right)^2\right]
\end{aligned}
\tag{S5}
$$

where G_{11}, G_{12}, G_{44}, and G'_{44} are the gradient coefficients. The gradient energy is the penalty for the spatially inhomogeneous polarization. The electrostatic energy density can be obtained through Legendre transformation, and is expressed as:

$$
f_{Electric} = -\frac{1}{2}\kappa_C\left(E_x^2 + E_y^2 + E_z^2\right) - \left(E_xP_x + E_yP_y + E_zP_z\right) \tag{S6}
$$

where, E_i ($i = x$, y, z) is the electric field due to the electrostatic potential distribution, and κ_c is dielectric constant of background material.

The temporal evolution for polarization or domain structure is calculated by the time-dependent Ginzburg-Landau equation

$$
\frac{\partial P_i(r,t)}{\partial t} = -L\frac{\delta F}{\delta P_i(r,t)} \tag{S7}
$$

where t represents time, L is the kinetic coefficient related to the domain mobility, $\delta F/\delta P_i\,(r,\ t)$ denotes the thermodynamic driving force for polarization evolution, and r is the spatial vector. In addition to the time-dependent Ginzburg-Landau equation, the following mechanical equilibrium equation

$$
\frac{\partial}{\partial x_i}\left(\frac{\partial f}{\partial \varepsilon_{ij}}\right) = 0 \tag{S8}
$$

and Maxwell's (or Gauss) equation

$$
\frac{\partial}{\partial x_i}\left(-\frac{\partial f}{\partial E_i}\right) = 0 \tag{S9}
$$

must be satisfied for charge and body force free ferroelectric materials simultaneously.

Using the variation or principal of virtual work, the governing Equations (S7)-(S9) are expressed in the integral form (or weak form) as [7]

$$\int_V \left\{ \frac{\partial f}{\partial \varepsilon_{ij}} \delta\varepsilon_{ij} + \frac{\partial f}{\partial E_i} \delta E_i + \frac{1}{L}\frac{\partial P_i}{\partial t} \delta P_i + \frac{\partial f}{\partial P_i} \delta P_i - \left(\frac{\partial f}{\partial P_{i,j}} \right) \delta P_{i,j} \right\} dV = \int_S \left\{ t_i \delta u_i - w d\phi + \pi_i \delta P_i \right\} dS \qquad \text{(S10)}$$

where t_i is the surface traction, w denotes surface charge, and $\pi_i = \frac{\partial f}{\partial P_{i,j}} n_j$ represents the surface gradient flux. A nonlinear finite element method [1] is employed to solve Eq. (S10), which is suitable for the arbitrary geometry of ferroelectric nanoporous structures.

III. The topological theory of defects applied to ferroelectric polarization structures

Ferroelectrics are characterized by spontaneous polarization, it is naturally to take a unit vector of polarization as the primary order parameter. The combination of the primary order parameters in a region constitutes an order parameter space [8]. To see the mapping of the polarization from real space on the order parameter space, one can take the angular direction of the polarization to describe the current state of topological structure in ferroelectric materials. This procedure can be viewed as mapping information in physical space into points in the order parameter space. For example, consider a rectilinear polarization domain, the order-parameter space in Fig. S3a can be taken as a circle: any possible values of polarization can be specified by an angle, and this angle, in turn, can be represented as a point on the circular order parameter space. Two other examples for the nonuniform polarization can be treated in similar manner, as shown in Fig. S3b and c. For polarization configuration observed in the present study, the order parameter space can also be taken as the circumference of a circle, namely the θ-space, where θ is defined as the angle that the polarization makes with an arbitrarily chosen direction; that is the *x*-axis in our consideration. In a non-uniform media the order parameter varies continuously except a singularity, known as a defect, where the order parameter is ill defined. The presence of topology defect can be observed infinitely far away in terms of the winding number, *n*, associated with the order parameter as one traverses around the singularity in a real system. In our case, it is the total angle θ that gets traversed when mapping the polarization vector with respect to the *x*-axis while completing a loop of any shape around the defect. In the other words, winding number counts how many times the polarization wraps around the circle.

Figure S4a shows different polarization profiles with a winding number of +1 because as one loops around them in counter clockwise (CCW) direction, the angle θ also completes one full circle in the same CCW direction. The initial phase shift differentiates the different polarization profiles even though their winding number is the same. For instance, CCW and clockwise (CW) polarization vortices have opposite chiralities as shown in Figure S4a at $\theta=\varphi+\pi/2$ and $\theta=\varphi-\pi/2$ respectively, they have the same $n=+1$. Similarly, Figure S4b shows different polarization profiles with a winding number of -1; one needs to rotate in the opposite direction in the θ-space with respect to the direction of rotation in the real space in order to map the polarization vector onto the θ-space.

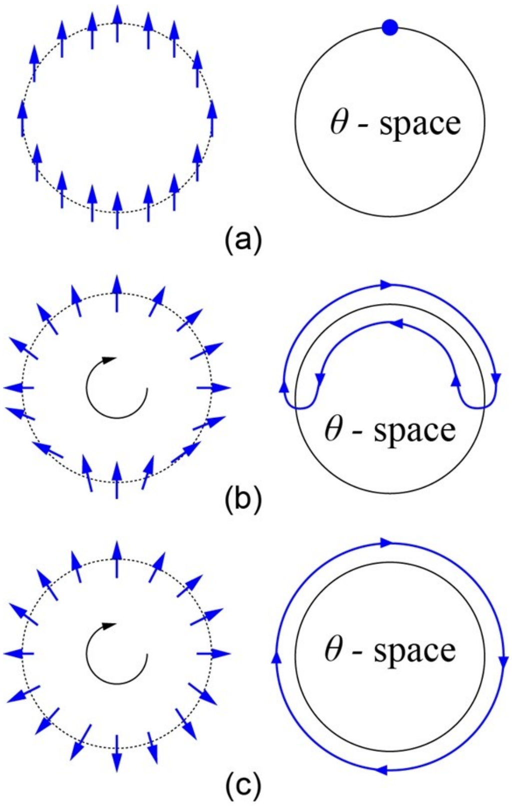
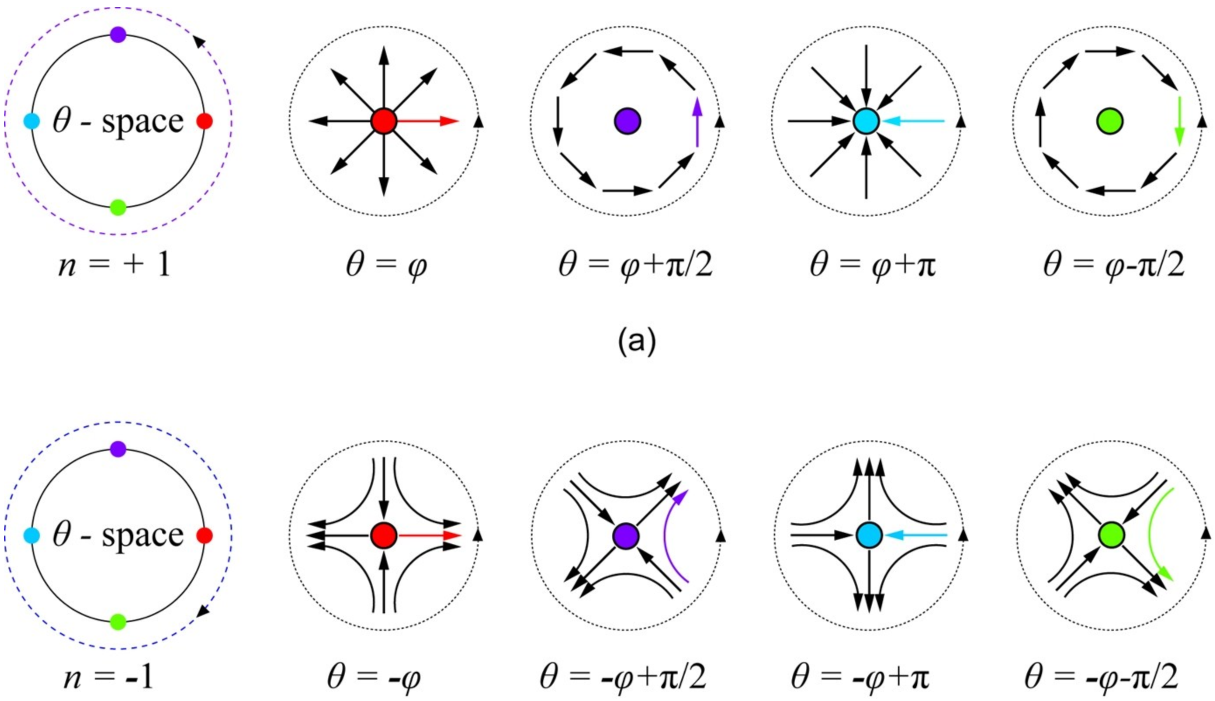


Figure S3. Polarization configurations on circular contours (left) and the maps they determine of the contours into order-parameter space (right). (a) The polarization is rectilinear over the entire contour. The contour can be mapped into a single point of order parameter space (zero winding number) [8]. (b) The nonuniform polarization over the contour: the resulting map of the contour into order-parameter space can be shrunk to a point (zero winding number) [8]. (c) The nonuniform polarization over the contour: the resulting map wraps the contour once around the circular order-parameter space (winding number 1).



(a)

(b)

Figure S4. Different polarization configurations for (a) n = +1 and (b) n = -1. Dashed black and purple circle indicate the direction of polarization traverse in real space and the direction of the θ traverse, respectively.

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