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Supplementary Material

Size dependent and distinguishing degenerated vortex states in ferroelectric nanodots under a controllable surface charge condition

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Table 1

Values of the material parameters in phase-field simulations (SI units and T in K).

α_1	α_{11}	α_{12}	α_{111}	α_{112}	α_{123}
$3.8(T-752)\times10^5$	-7.3×10^7	7.5×10^8	2.6×10^8	6.1×10^8	-3.7×10^9
Q_{11}	Q_{12}	Q_{44}	s_{11}	s_{12}	s_{44}
0.089	–0.026	0.03375	8.0×10^{-12}	-2.7×10^{-12}	9.24×10^{-12}
G_{11}	G_{12}	G_{44}	$G_{44}^{'}$	δ_i^{eff}	ε_b
3.46×10^{-10}	0	1.73×10^{-10}	1.73×10^{-10}	5×10^{-9}	4.425×10^{-10}
P_0					
0.757					

Phase diagram during the process of increasing surface charge density

To have a comprehensive insight into the effects of temperature and surface charges, we conduct a series of simulations on the domain evolution of the nanodots with degenerated vortex states under different temperatures during the process of increasing surface charge density σ. For the nanodots with initial <100>, <010> or <001> vortex state, the phase diagrams of the evolved domain pattern as a function of temperature and σ are depicted in Figs. S1a, S1b and S1c, respectively. For the nanodot with <100> vortex state as shown in Fig. S1a, a vortex-polar state forms at T=0K after placing two parallel electrodes along <100> direction, which is similar to the result of T=300K. This vortex-polar state remains in the ferroelectric nanodot when σ is not larger than 0.4C/m^2. Then, with the increasing of σ, a single c-domain state (i.e. $|\overline{P_3}| >> |\overline{P_1}|$ and $|\overline{P_2}|$) will form. Similar evolution paths can be observed under other higher temperatures, yet with a decreasing stability of vortex-polar state. As the temperature reaches 500K, the vortex-polar state becomes unstable and changes to single c-domain state when σ is no less than 0.1C/m^2. From Fig. S1a, the vortex-polar state is stable under lower surface charge densities while a single c-domain state favors to form under higher surface charge densities under all simulated temperatures. The critical σ between the two states decreases from 0.4 to 0.1C/m^2 when temperature increases from 0 to 500K.

In the nanodot with an initial <010> vortex state (see Fig. S1b), more abundant domain patterns have been obtained. Overall, seven domains are observed in the simulation. Vortices favor to form under low surface charge densities and low

temperatures, and the single *c*-domain state is stable under high surface charge densities. In detail, the vortex state along <010> direction remains stable after placing electrodes at *T*=0 and 100K. Then, the vortex core shifts to the side surface during the process of increasing σ. At σ of about 0.25C/m^2, the toroidal order disappears in the nanodot, and a nonzero polarization of $|\overline{P_1}|$ generate in the nanodot. This indicates that the electric field generated by surface charges is not enough to lead the formation of a single *c*-domain state at *T*=0 and 100K. With a further increase of σ, a *c*-domain state forms in the nanodot. With the placement of two electrodes, vortex keeps at *T*=200K, while a 180° domain pattern forms at *T*=300 and 400K. Then, similar evolution paths are observed under these temperatures. Same with nanodot under lower temperatures, the vortex core of nanodot shifts to a side with the increase of σ. An *ac*-domain (i.e. $|\overline{P_1}|$ and $|\overline{P_3}|>>|\overline{P_2}|$) state forms directly when vortex disappears during increasing σ. Finally, with a further increase of σ, the *c*-domain state is stable in the nanodot. When the temperature increases to 500K, an *a*-domain state (i.e. $|\overline{P_1}|>>|\overline{P_3}|$ and $|\overline{P_2}|$) forms when placing electrodes. Then $|\overline{P_3}|$ increases with σ, indicating the domain patterns change from *a*-domain state to *ac*-domain state. When σ increases to 0.2C/m^2, $|\overline{P_1}|$ decreases to zero and *c*-domain state forms in the nanodot.

For the nanodot with <001> vortex state shown in Fig. S1c, after placing electrodes, initial vortex patterns with <001> direction keep under temperatures lower than 200K. Under these temperatures, $|\overline{P_3}|$ increases with the increase of σ. Nonzero polarization $|\overline{P_3}|$ and nonzero toroidal moment $|g_z|$ indicate that a polar-vortex state

exists in the nanodot. This polar-vortex state keeps under high surface charge densities, even σ=1C/m^2. Under the condition of T=300K and T=400K, a 180° domain forms after placing of two electrodes. With the increase of σ, a *c*-domain state forms when σ is larger than 0.26C/m^2 at T=300K. Under T=400K, an *ac*-domain state forms and finally *c*-domain state is stable in the nanodot., When the temperature reaches 500K, an *a*-domain state forms directly after placing the electrodes to the two parallel surfaces on <100> direction. Then, with the increase of σ, an *ac*-domain forms in the nanodot and finally the *c*-domain state forms.

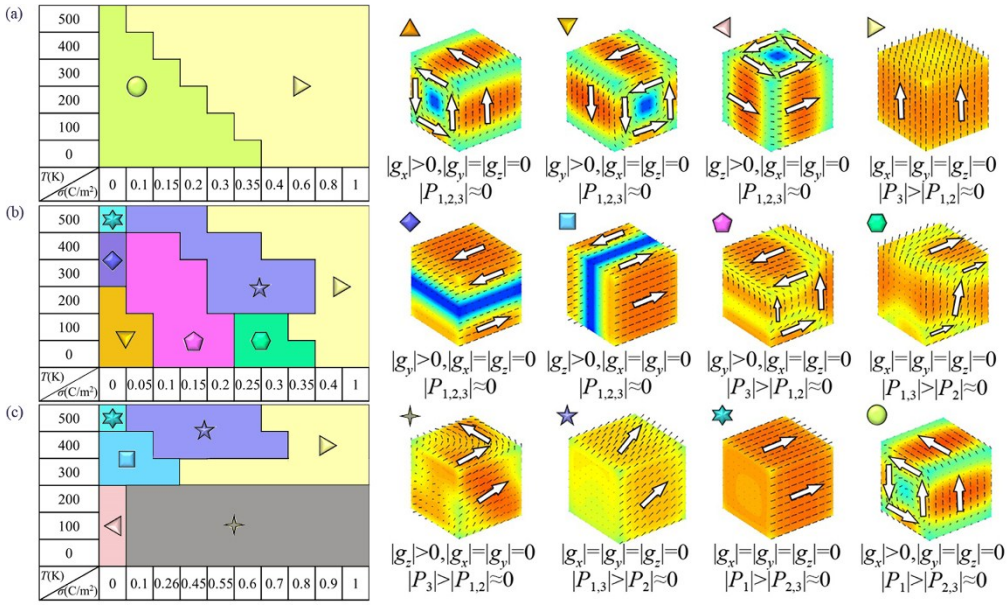

Fig. S1 Phase diagrams of a nanodot with different initial vortex state as a function of temperature and increasing σ. (a) Nanodot with <100> vortex state, (b) nanodot with <010> vortex state and (c) nanodot with <001> vortex state.

Phase diagram during the process of decreasing surface charge density

The phase diagrams of temperature and decreasing σ are summarized in Fig. S2, which depict the domain structure of the nanodot as functions of temperature and decreasing σ. The domain structures under σ=1C/m^2 are obtained in the process of increasing σ.

For the nanodot with <100> vortex state (see Fig. S2a), under all simulated temperatures, *c*-domain state forms under σ=1C/m^2, and it keeps in the nanodot until σ decreases to 0.2C/m^2. At temperatures lower than 400K, a polar-vortex state forms. With a further decrease of σ, a polar-vortex state with another pattern forms in the nanodot. At *T*=400 and 500K, *ac*-domain state forms when σ is lower than 0.2C/m^2. The polar-vortex state forms with the decrease of σ. Finally, under all temperatures, vortex along <100> direction forms in the nanodot after removing electrodes.

As shown in Fig. S2b, similar with the nanodot with <100> vortex state, *c*-domain state forms under σ=1C/m^2 at all simulated temperatures in the nanodot with <010> direction. When temperature is lower than 300K, 90° domain pattern exists in the nanodot during the process of decreasing σ. When surface charges are all removed, vortex with <010> orientation forms in the nanodot. At *T*=300 and 400K, *c*-domain state transforms to *ac*-domain state, and finally is stable at *a*-domain state with the decrease of σ. When temperature reaches 500K, *c*-domain state keeps if there are surface charges bonded on the surfaces. The *a*-domain state forms when surface charges are all removed. Lastly, after removing electrodes, vortex along <010> direction forms under all temperatures.

In the nanodot with <001> vortex state (see Fig. S2c), A polar-vortex state forms under temperatures lower than 300K, and *c*-domain state exists at *T*=300K, 400K and 500K. When temperature is lower than 300K, the polar-vortex state keeps in the nanodot if there are surface charges. When surface charges are moved, vortex reconstructs. Under the condition of *T*=300K and 400K, *ac*-domain state forms when σ decreases to 0.24C/m^2 and 0.15C/m^2. After removing surface charges, a single *a*-domain state keeps in the nanodot. For the nanodot at *T*=500K, *c*-domain state is stable in the nanodot if there is surface charge and *a*-domain state forms under the condition of σ=0. With the remove of electrodes, vortex with <001> orientation reconstructs in the nanodot, indicating that the initial domain structure is not destroyed in the process of increasing σ.

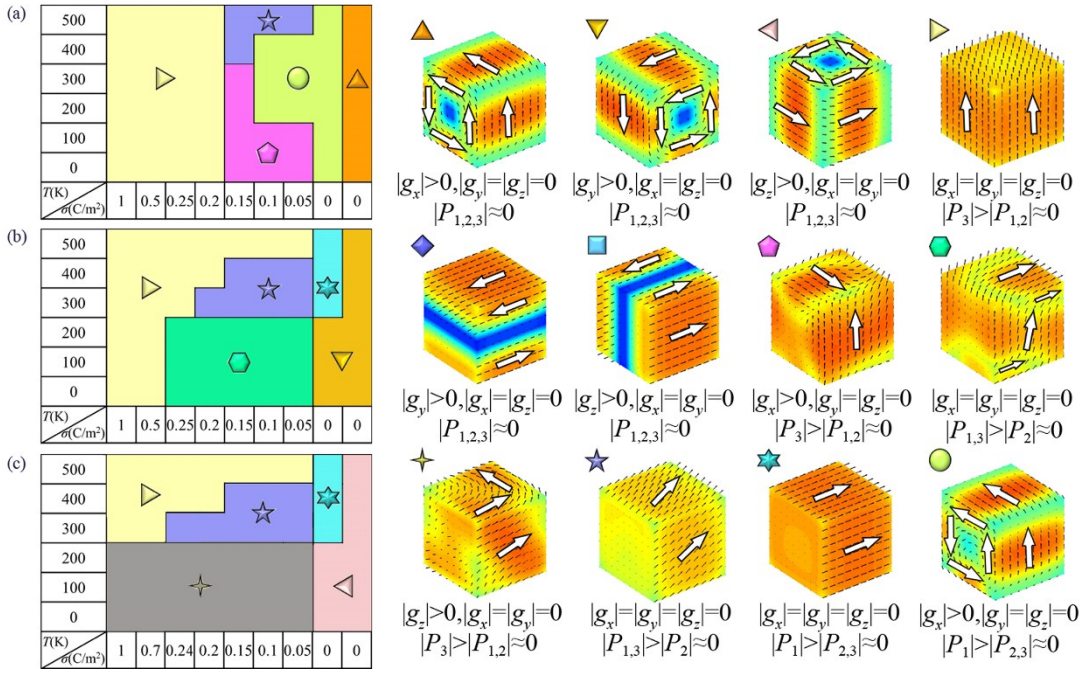

Fig. S2 Phase diagrams of a nanodot with different initial vortex state as a function of temperature and decreasing σ. (a) Nanodot with <100> vortex state, (b) nanodot with <010> vortex state and (c) nanodot with <001> vortex state.