Electronic Supplementary Material (ESI) for Nanoscale.
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Supplementary Materials for

Ferroelectricity of ice nanotube forests grown in three-dimensional graphene: electric field effect

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Supplementary Figure S1-S2

References

1. Three-dimension (3D) graphene fixed/unfixed

Animation M1 is vivid to study the influence of deformation of three-dimensional (3D) graphene container on the growth of ice NTs. Water molecules were cooled from 400 K to 100 K at a rate of 3 K/ns and then quenched to very low temperatures (close to 0 K) at a rate of 50 K/ns. The results demonstrated that the 3D graphene as a rigid body did not affect the normal growth of ice NTs, but it could help greatly improve the calculation speed.

2. Growth of ice nanotubes (NTs) with ferroelectricity

Animation M2 describes the formation of (5, 0) ice NT arrays in 3D graphene. Here the 3D graphene container is absent for clarity. Besides, the change of ferroelectricity with time during the formation of ice NTs is also given.

3. Electric field effect on the already obtained ice NTs

Animation M3 depicts that the electric field of 0.5 V/Å was directly applied to the axial direction of a (5, 0) ice NT. The results revealed that each water molecule of the ice NT was rearranged along the direction of the electric field, which greatly improved the ferroelectricity of the structure.

4. Growth of spiral ice NTs under electric field applied during the cooling process

Animation M4 describes the application of an electric field of 0.5 V/Å to the cooling process of water molecules from 400 K to 100 K and then the system was quenched to an extremely low temperature (close to 0 K) at a rate of 50 K/ns. The results showed that the spiral ice NTs were formed under the action of electric field during the cooling process, and the obtained tube index was confirmed to be (5, 1).

This was obviously different from the situation without electric field. The structure of the ice NT had changed significantly with ferroelectricity greatly improved.

5. Ferroelectricity of ice NT inside a carbon nanotube (CNT)

To check our simulation results and prove the superiority of generating ice NTs forests in 3D graphene proposed here, a (5, 0) ice NT grown in (15, 0) CNT[1] was reproduced here under the same simulation conditions. The temperature dependence of ferroelectricity of the water molecules system during the cooling and melting processes is given in Fig. S1 which is in good agreement with previous work[1]. A similar first-order phase transition occurred during the growth and melting processes thus forming an analogous narrow hysteresis loop area. The ferroelectricity of (5, 0) ice NT formed after the cooling process was calculated to be $P_z = 0.34\,\text{eÅ}$ which was the same as that of the selected representative ice NT formed in 3D graphene.

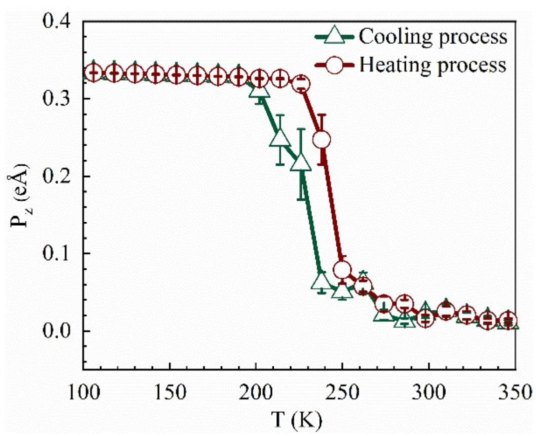

Figure S1. Temperature dependence of ferroelectricity of (5, 0) ice NT grown in (15, 0) CNT during the cooling and heating processes.

From analysis above, ferroelectric (5, 0) ice NT could be formed in both (15, 0) CNT and 3D graphene (*d*CHC-2). The confined water molecules both underwent a paraelectric-ferroelectric first-order phase transition. The ferroelectricity of the formed ice NTs originated from the combination of spatial constraints, ice rules and the unique hydrogen bond orientation order in ice NTs, which forced the inherent dipole moment of water molecules to be ordered[2-4]. From the structure point of view, the equivalent diameter of each hole of the 3D graphene (*d*CHC-2) was very close to that of the (15, 0) CNT, so 3D graphene could be viewed as a collection of multiple CNTs. Therefore, the ice NTs grown in the two containers were essentially the same both of which have (5, 0) tube indices.

6. Growth of different ice NTs forest types

In order to obtain other types of ferroelectric ice NTs, triangular ice NTs were grown by using the special structure of triangular 3D (t3D) graphene as shown in Fig. S2(a)[5, 6]. Additionally, animation M5 indicates that triangular t3D graphene could also be used as a container to grow ice NTs. The results demonstrated that (3, 0) ice NTs could indeed grow inside.

In addition, the pore sizes of 3D graphene may not be uniformly and perfectly the same in real synthesis experiments[7-9] so that ice NTs with different edge numbers could be generated during a once growth process. In this paper, (2, 2)-type non-equilateral hexagonal 3D graphene (HGN(2, 2)) was employed to simultaneously grow triangular ice (3, 0) NTs and pentagonal (5, 0) ice NTs (*c.f.* Fig. S2(b)) [8]. Besides, animation M6 displays the confinement effect of HGN (2, 2) graphene containers with different pore sizes on the growth of ice NTs. The results illustrated that triangular (3, 0) ice NTs and pentagonal (5, 0) ice NTs could grow in the different holes of 3D graphene.

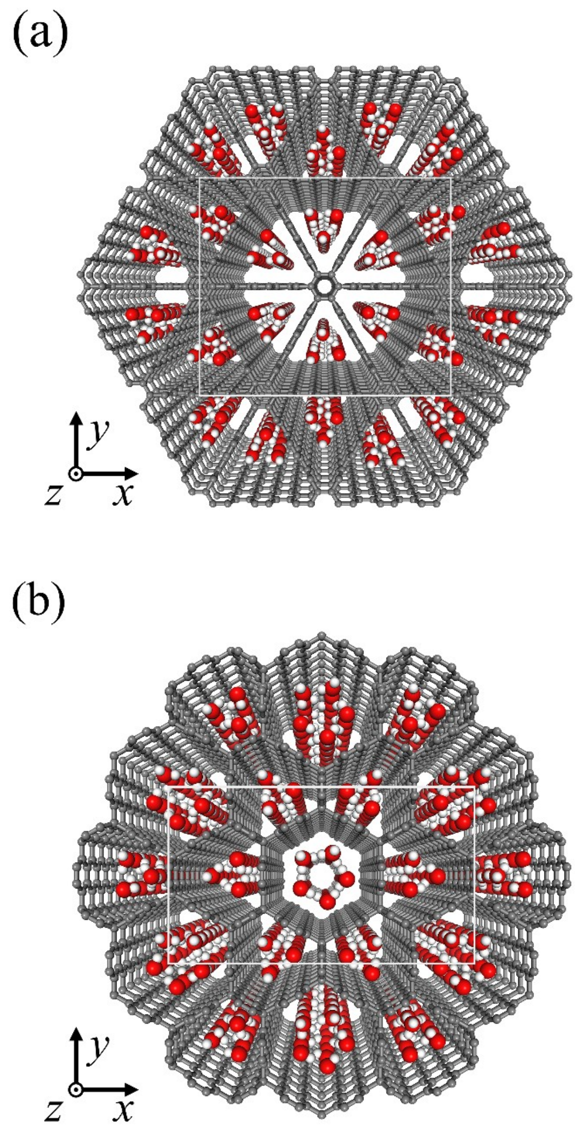

Figure S2. (a) (3, 0) ice NTs forest formed in t3D graphene. (b) Both (3, 0) ice NTs and (5, 0) ice NTs forest formed simultaneously in HGN (2, 2).

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