Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information (ESI)

Rich topologies of monolayer ices via unconventional electrowetting

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Captions of Supplemental Movies:

Movie S1. The instantaneous formation process of 6^3 ML ice at 300 K on the model substrate by MD simulation.

Movie S2. The instantaneous formation process of $4•8^2$ ML ice at 300 K on the model substrate by MD simulation.

Movie S3. The instantaneous formation process of 4•6•12 ML ice at 300 K on the model substrate by MD simulation.

Movie S4. The instantaneous formation process of 4•6•12 ML ice at 300 K on the graphene model surface with fixed positive-negative charges by MD simulation.

Movie S5. The trajectory of $4•6^2$ ML ice on the modified diamond (100) surface at 150 K by AIMD.

Movie S6. The trajectory of 4•6•12 ML ice on the boron and nitrogen doped graphene surface at 200 K by AIMD.

1. Dipoles and quadrupoles distributions on the substrates.

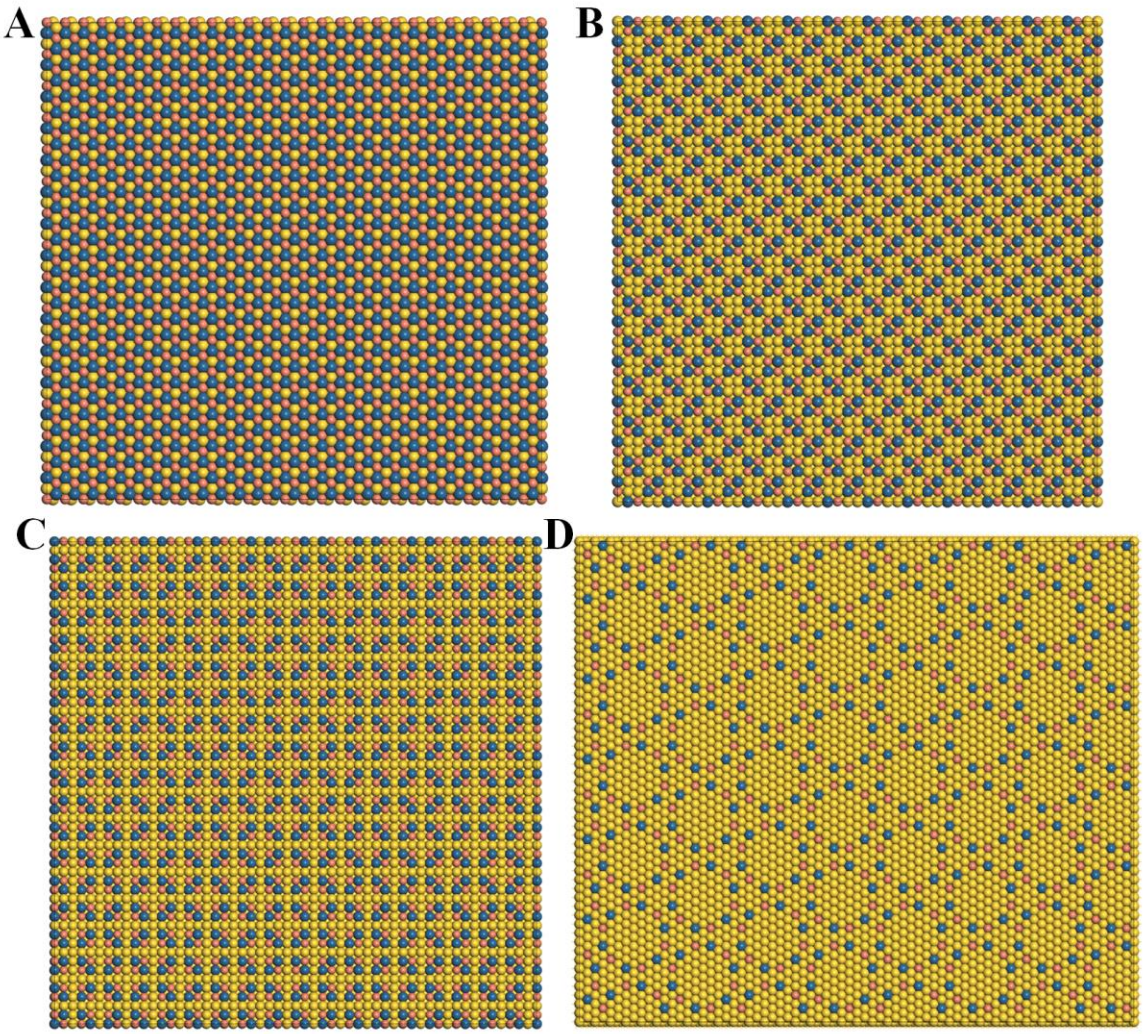

Fig. S1 (**A**) Dipoles distribution on the substrates of 6^3 ML ice, (**B**) quadrupoles distribution on the substrates of $4•8^2$ ML ice, (**C**) quadrupoles distribution on the substrates of $4•6^2$ ML ice, (**D**) quadrupoles distribution on the substrates of 4•6•12 ML ice. Note: The atomic arrangement of the substrate resembles the structure of Au (111) and Au (100). Except the substrate of the 6^3 case keeping the original Au lattice, the substrates of the $4•8^2$, $4•6^2$, and 4•6•12 cases are compressed by 17%, 20%, and 48%, respectively, in comparison with the original Au to make the average length of positive-negative charges around 2.8 Å. Pink and light blue atoms are charged by ±q, yellow atoms are neutral atoms.

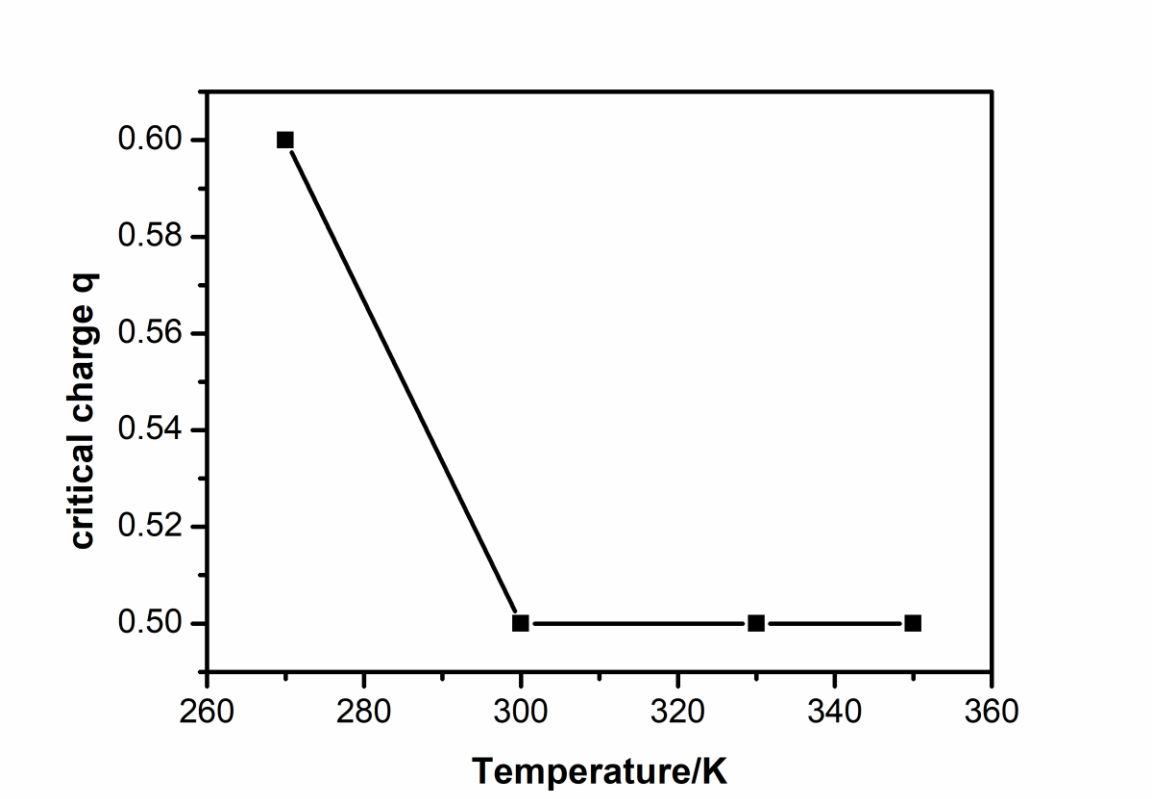

Fig. S2 The critical charge *q* required for the monolayer ice spontaneously forming at different temperature.

2. The 4•6•12 ML ice spontaneously formed at 300 K on the graphene model surface (10.23 nm × 8.86 nm) with distributed quadrupoles.

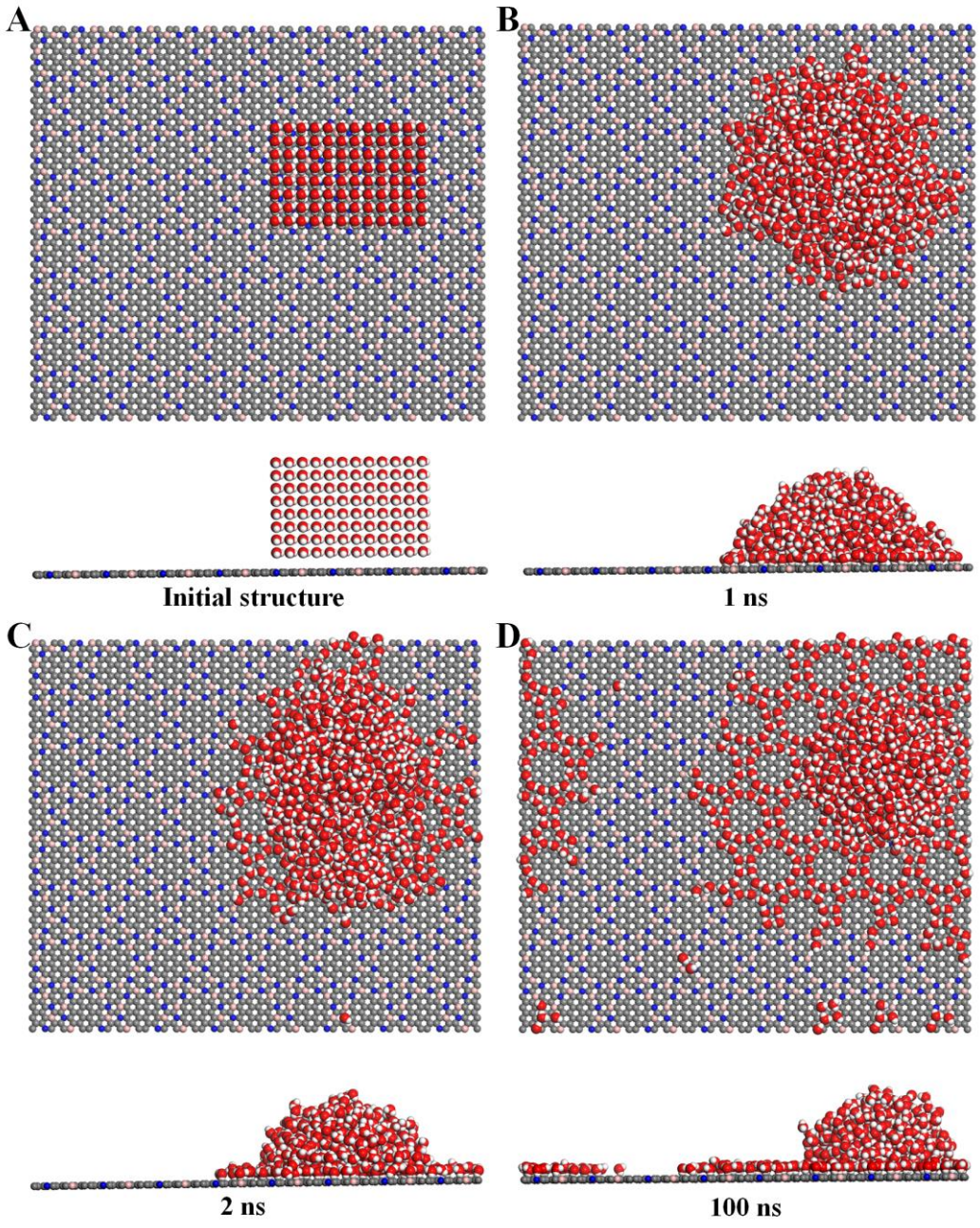

Fig. S3 Structure snapshots of spontaneous formation of the 4•6•12 ML ice at 300 K on the graphene model surface. (A) initial structure, (B) structure at 1 ns, (C), structure at 2 ns, and (D) structure at 100 ns. Note: The light pink and blue atoms are charged by ±0.6 e, the upper one is the top view of the structure, and the lower one is the side view of the structure in each figure. The interaction between carbon atoms and water molecules is represented by a 12-6 Lennard-Jones (LJ) potential with parameters 3.2 Å for $\sigma_{C\text{-}O}$ and 0.1 kJ/mol for $\varepsilon_{C\text{-}O}$.

3. Snapshots of each ML ices in the heating processes from a low temperature.

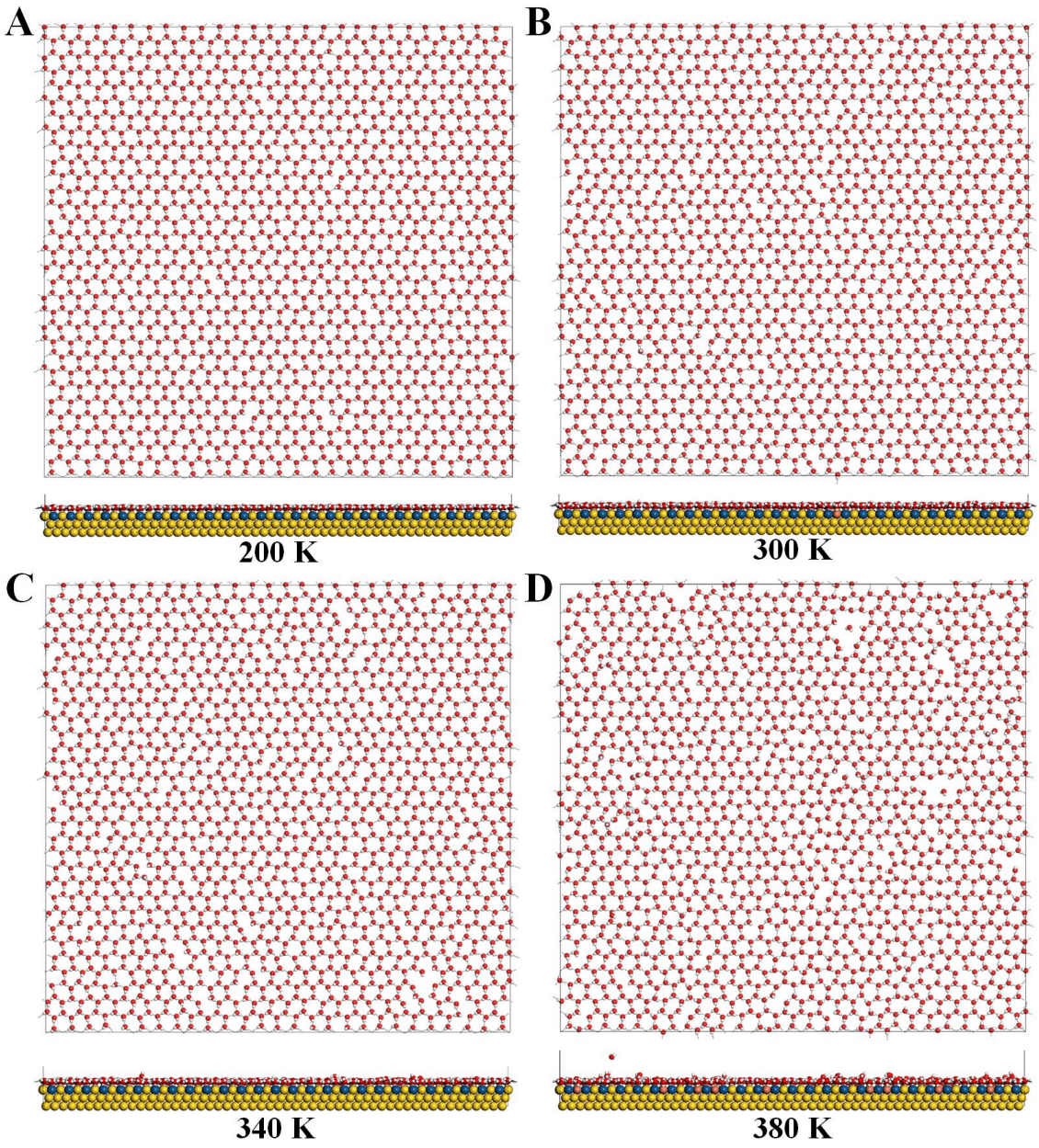

Fig. S4 Structure snapshots of 6^3 ML ice at the time of 5 ns and at various temperature: (**A**) 200 K, (**B**) 300 K, (**C**) 340 K, (**D**) 380 K. Note: The atomic arrangement of the substrate resembles the structure of Au (111), pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the upper one is the top view of the structure with substrate unseen, and the lower one is the side view of the structure in each figure.

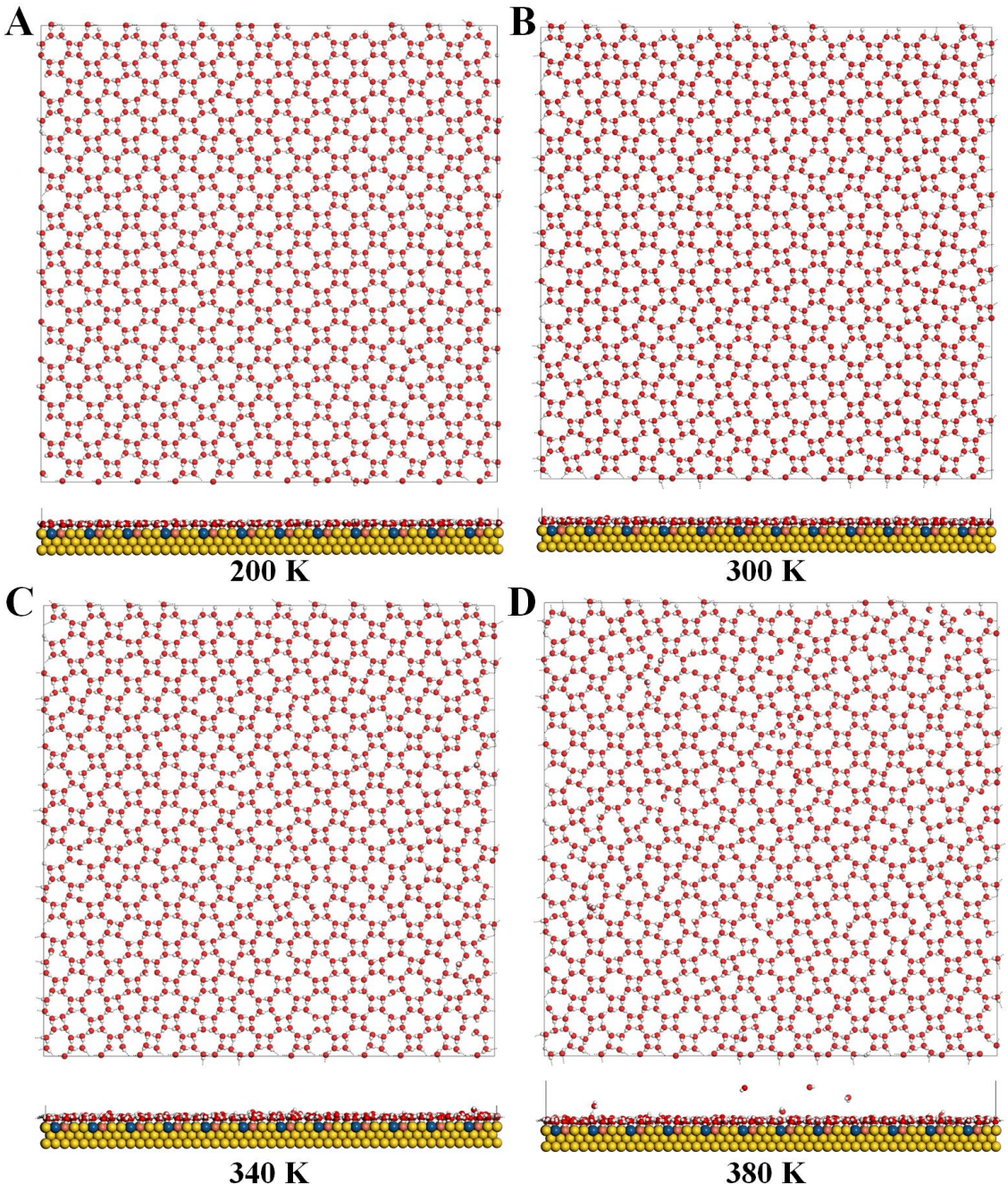

Fig. S5 Structure snapshots of $4•8^2$ ML ice at the time of 5 ns and at various temperature: (**A**) 200 K, (**B**) 300 K, (**C**) 340 K, (**D**) 380 K. Note: The atomic arrangement of the substrate resembles the structure of Au (100) with 17% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the upper one is the top view of the structure with substrate unseen, and the lower one is the side view of the structure in each figure.

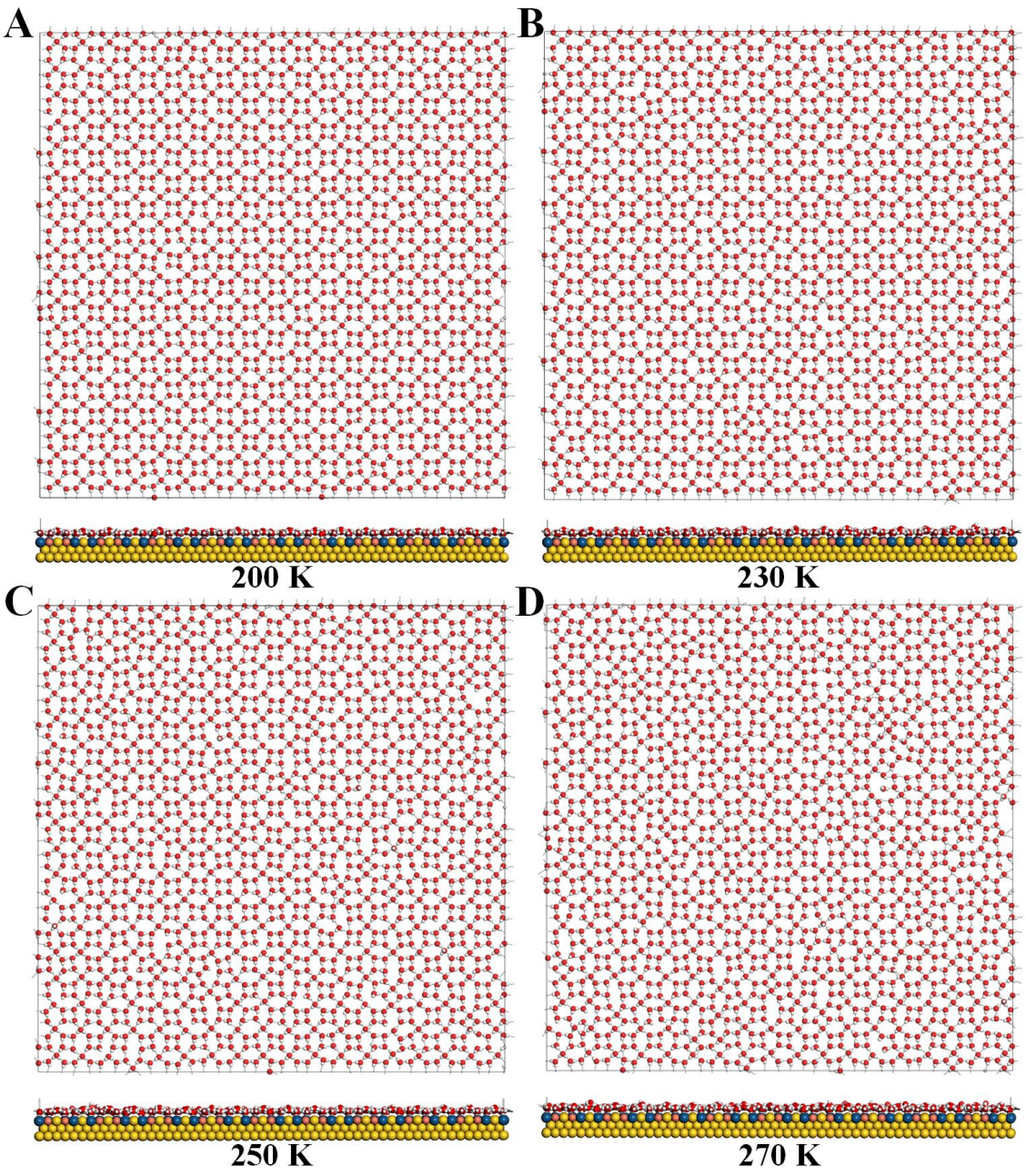

Fig. S6 Structure snapshots of 4•6^2 ML ice at the time of 5 ns and at various temperature: (**A**) 200 K, (**B**) 230 K, (**C**) 250 K, (**D**) 270 K. Note: The atomic arrangement of the substrate resembles the structure of Au (100) with 20% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the upper one is the top view of the structure with substrate unseen, and the lower one is the side view of the structure in each figure.

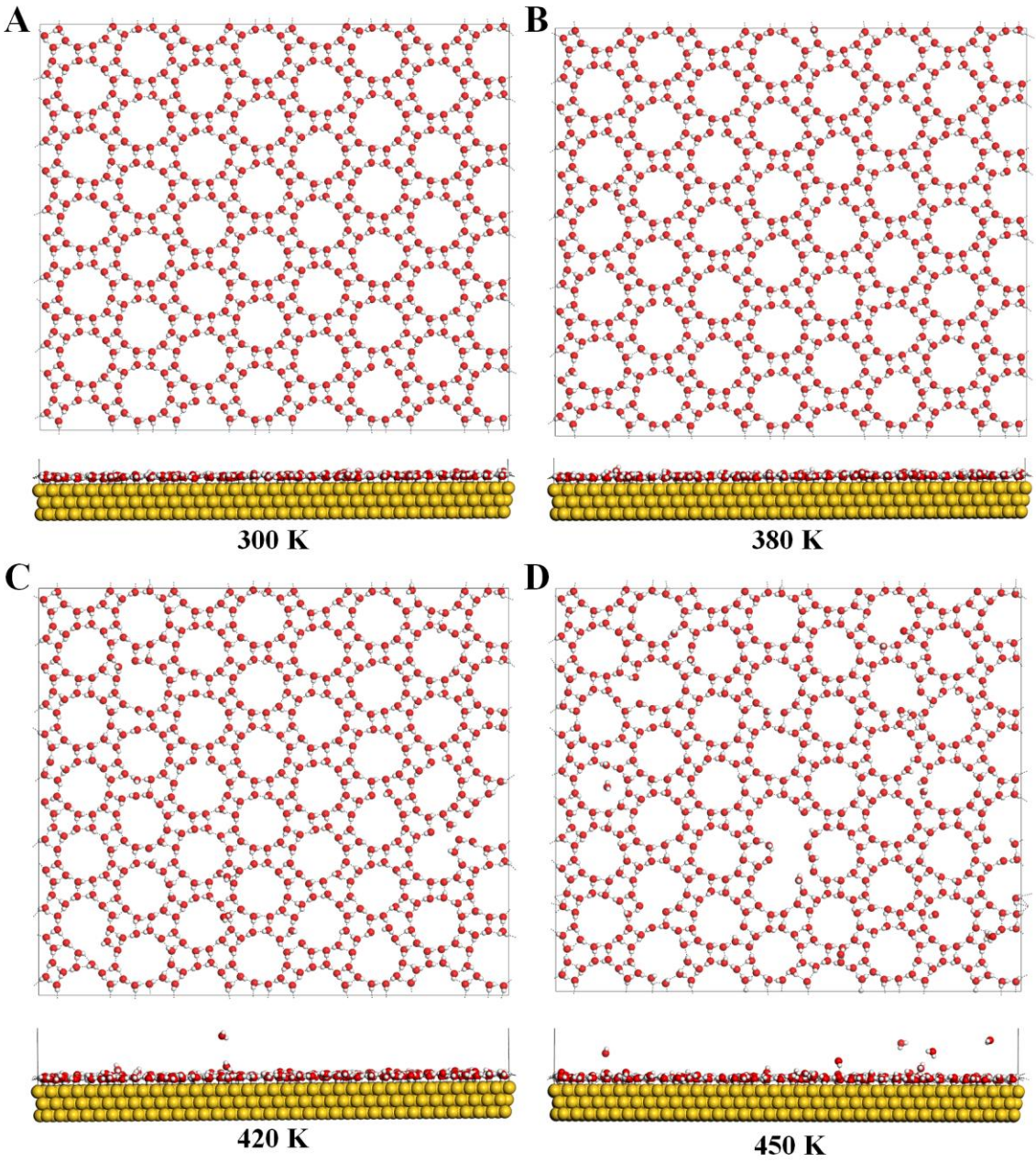

Fig. S7 Structure snapshots of 4•6•12 ML ice at the time of 5 ns and at various temperature: (**A**) 300 K, (**B**) 380 K, (**C**) 420 K, (**D**) 450 K. Note: The atomic arrangement of the substrate resembles the structure of Au (111) with 48% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the upper one is the top view of the structure with substrate unseen, and the lower one is the side view of the structure in each figure.

4. Snapshots of each ML ices in the cooling processes from a high temperature.

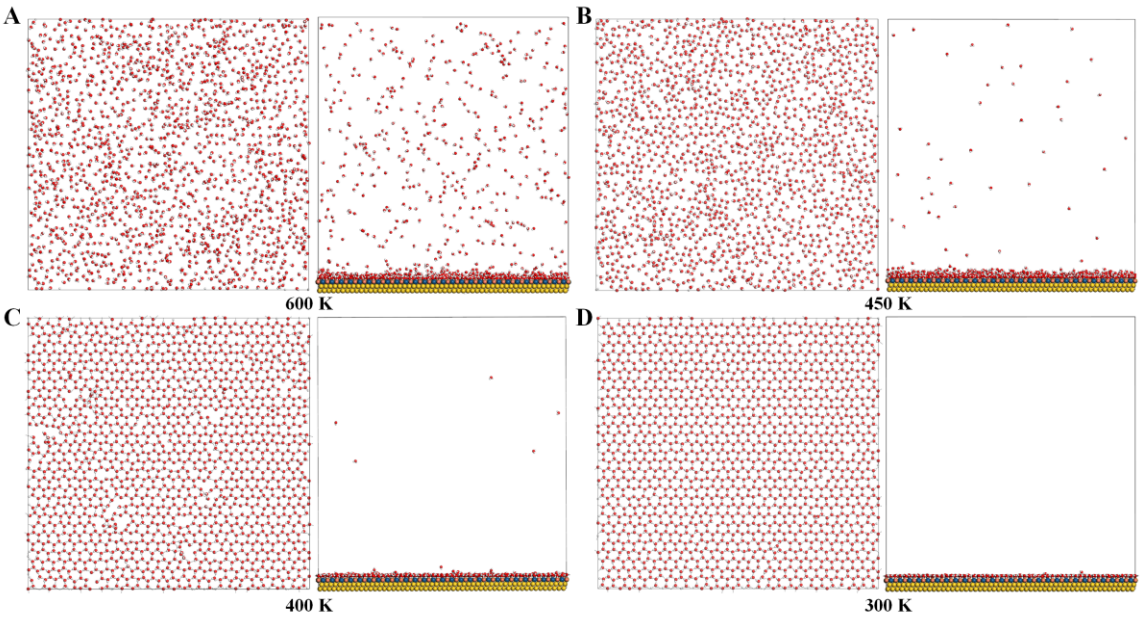

Fig. S8 Structure snapshots of 6^3 ML ice at the time of 5 ns and at various temperature: (**A**) 600 K, (**B**) 450 K, (**C**) 400 K, (**D**) 300 K. Note: The atomic arrangement of the substrate resembles the structure of Au (111); pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the left one is the top view of the structure with substrate unseen, and the right one is the side view of the structure in each figure.

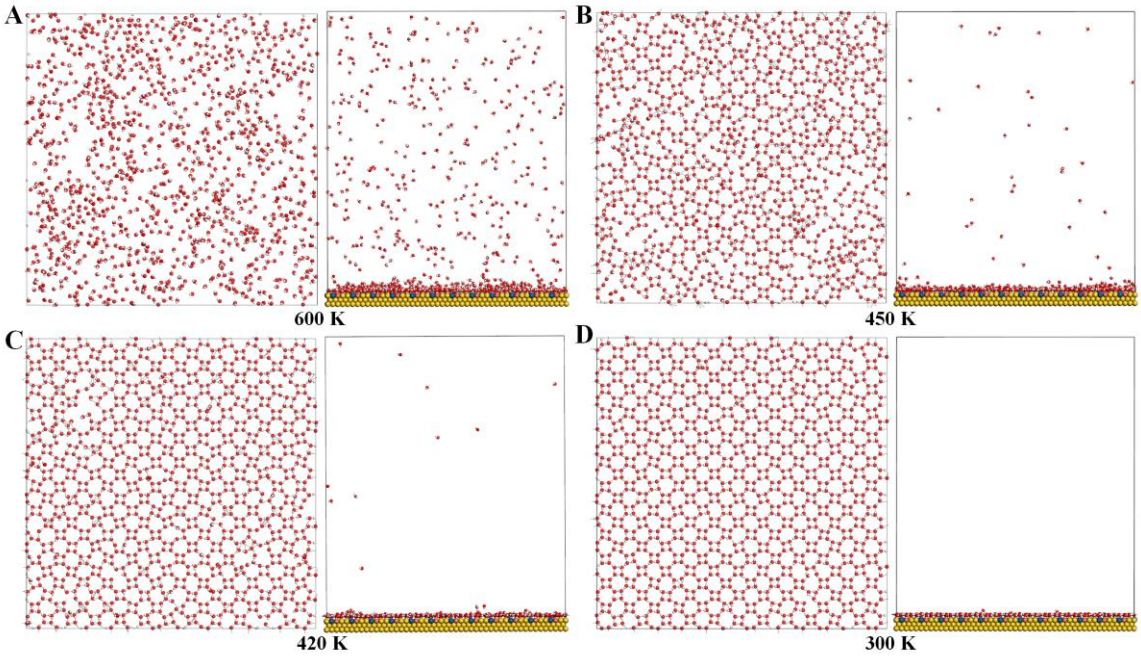

Fig. S9 Structure snapshots of $4•8^2$ ML ice at the time of 5 ns and at various temperature: (**A**) 600 K, (**B**) 450 K, (**C**) 420 K, (**D**) 300 K. Note: The atomic arrangement of the substrate resembles the structure of Au (100) with 17% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the left one is the top view of the structure with substrate unseen, and the right one is the side view of the structure in each figure.

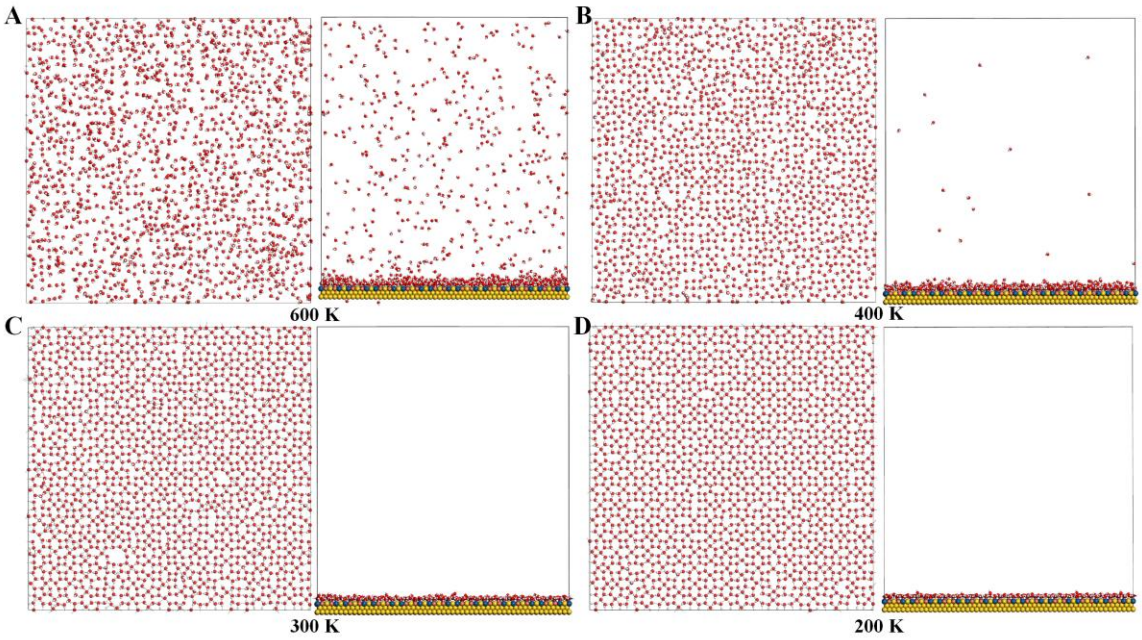

Fig. S10 Structure snapshots of $4•6^2$ ML ice at the time of 5 ns and at various temperature: (**A**) 600 K, (**B**) 400 K, (**C**) 300 K, (**D**) 200 K. Note: The atomic arrangement of the substrate resembles the structure of Au (100) with 20% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the left one is the top view of the structure with substrate unseen, and the right one is the side view of the structure in each figure.

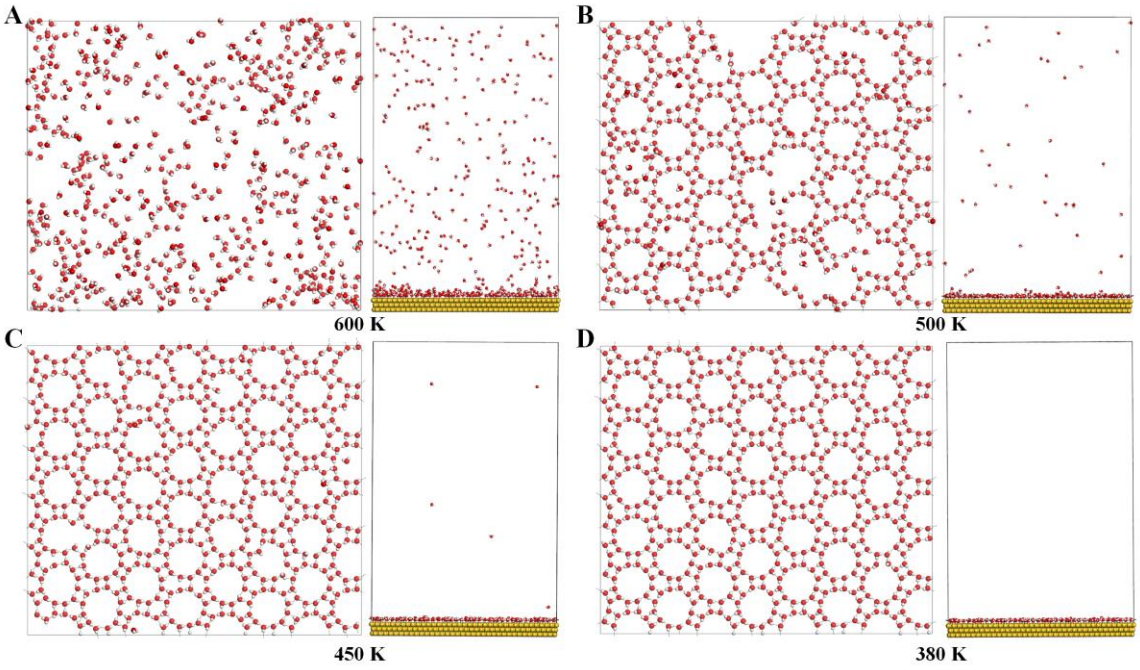

Fig. S11 Structure snapshots of 4•6•12 ML ice at the time of 5 ns and at various temperature. (**A**) 600 K, (**B**) 500 K, (**C**) 450 K, (**D**) 380 K. Note: The atomic arrangement of the substrate resembles the structure of Au (111) with 48% compression comparing to the original Au lattice to make the average length of positive-negative charges around 2.8 Å; pink and light blue atoms are charged by ±q, and yellow atoms are neutral atoms. To make it more clear, the left one is the top view of the structure with substrate unseen, and the right one is the side view of the structure in each figure.

5. For the realization of the unreported 4•6^2 and 4•6•12 ML ices on a realistic material surface.

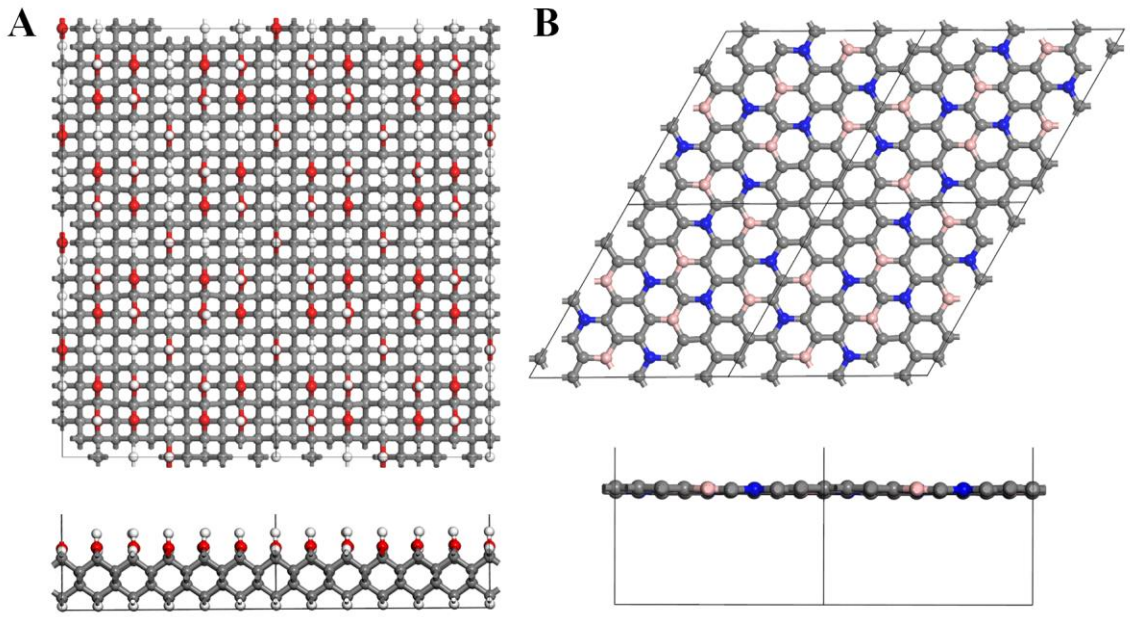

Fig. S12 A realistic substrate which may be used to realize the 4•6^2 and 4•6•12 ML ices. (**A**) Unit cell (shown by 2×2) of H-terminated surface of diamond (100) with OH and O modification at certain positions. (**B**) Unit cell (shown by 2×2) of graphene surface with boron and nitrogen atoms doped at certain positions. Note: To make it more clear, the upper one is the top view of the structure, and the lower one is the side view of the structure in each figure. Red and white balls represent oxygen and hydrogen atoms, respectively. Grey, blue, and light pink balls represent carbon, nitrogen, and boron atoms, respectively. The solid black line represents the lattice of the unit cell.